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# CHEMISTRY.

BY

LEOPOLD GMELIN.

VOL. XI.

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## ORGANIC CHEMISTRY,

### VOL. V.

ORGANIC COMPOUNDS CONTAINING TEN AND TWELVE ATOMS OF CARBON.

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TRANSLATED BY

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# TEN-CARBON COMPOUNDS

(*Continued*).

## AMYLENE SERIES.

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### A. Primary Series.

### Primary Nucleus. Amylene, $C^{10}H^{10}$.

Balard. (1844). *N. Ann. Chim. Phys.* 12, 320.
Frankland. *Ann. Pharm.* 74, 41.

*Valerene* (Kolbe); *Myle* (Gm.)—The amylene of Cahours is however $C^{20}H^{20}$.

*Formation and Preparation.* 1. Potato fusel-oil is distilled with a very concentrated aqueous solution (70° Bm.) of chloride of zinc in a retort, the ebullition taking place at about 130°; the resulting distillate, which is a mixture of $C^{10}H^{10}$, $C^{20}H^{20}$ and $C^{40}H^{40}$, rectified, with change of receiver, the boiling point rising from 60° to 300°; and the portion which first passes over, shaken up with oil of vitriol, whereupon the pure amylene rises to the top when the liquid is left at rest, the higher compounds remaining dissolved in the oil of vitriol. (Balard.) — 2. Chloride of amyl, $C^{10}H^{11}Cl$, is distilled with the potash-lime. (Balard.) — 3. A strong glass tube, $\frac{3}{4}$ of an inch wide and 14 inches long, is filled to the depth of $1\frac{1}{2}$ inch with pasty zinc-amalgam, above which is placed a two-inch layer of granulated zinc (which likewise unites with the mercury, as the zinc in the amalgam is used up), and then 6 or 8 drachms of iodide of amyl; the tube drawn out at top to a very fine point; the air driven out by heating the iodide of amyl to the boiling point; the neck sealed; the tube immersed in sand three inches deep, and heated for some hours to 160° — 180°; and the point broken off after the tube has cooled. Potassium, to the amount of 1 or 2 grammes, is then introduced; the tube again sealed, heated for an hour, and connected by means of a cork, after it has cooled and the point has been broken off, with a distillation-tube leading into a receiver surrounded with a freezing mixture; — then heated to 80° in the water-bath, whereupon $\frac{2}{3}$ of the product passes over; and finally over the flame of a spirit-lamp, whereby the last third of the

distillate, consisting of $C^{10}H^{11}$ [$C^{20}H^{22}$] is obtained. The first two-thirds of the distillate, which passes over at 80°, is a mixture of $C^5H^5$ and $C^5H^6$ [amylene $C^{10}H^{10}$ and hydride of amyl $C^{10}H^{12}$]. This mixture contains 84·2 p.c C and 15·9 H (excess 0·1); it boils at the heat of the hand, and exhibits a vapour-density of 2·419; it has a pungent, rather unpleasant odour, somewhat like that of butylene; its taste is rather sweet at first, but afterwards unpleasant and tarry. Fuming oil of vitriol brought in contact with 100 vol. of the gas, condenses 46·78 vol. of it, consisting of amylene-vapour, that is to say about one-half. (Frankland.)

[There is no method given for obtaining amylene in the free state from this mixture; and Frankland appears to have deduced the properties of pure amylene merely from those of the mixture.]

¶ 4. Sulphamylate of lime heated above 100° turns soft, blackens, and gives off a combustible gas mixed with a considerable quantity of sulphurous and carbonic acid. On passing this gas through milk of lime, and collecting the remaining portion over water, a colourless, volatile combustible liquid collects on the surface of the water; and this, after washing with water and carbonate of soda, and drying over chloride of calcium, yields amylene. As the heat increases, the quantity of amylene obtained diminishes, and a yellowish less volatile liquid is obtained, consisting partly of amylic ether (p. 7.) (Kekulé, *Ann. Pharm.* 75, 275.) ¶

*Properties.* Transparent, colourless, very thin liquid, having the odour of putrid cabbage; boils at 39°. Vapour-density 2·68°. (Balard.) — Transparent, colourless liquid, boiling at about 35°; having a vapour-density of about 2·386; odour penetrating and disagreeable, recalling that of butylene. (Frankland.) — Boiling point 42°; vapour-density 2·43. (Kekulé.) It is used as an anæsthetic agent.

| | | | | | Balard. | | | | Kekulé. |
|---|---|---|---|---|---|---|---|---|---|
| 10 C | 60 | .... | 85·71 | .... | 84·15 | .... | 83·5 | | |
| 10 H | 10 | .... | 14·29 | .... | 14·70 | .... | 14·7 | .... | 14·4 |
| $C^{10}H^{10}$ | 70 | .... | 100·00 | .... | 98·85 | .... | 98·2 | | |

| | Vol. | | Density. |
|---|---|---|---|
| C-vapour | 10 | ................ | 4·1600 |
| H-gas | 10 | ................ | 0·6930 |
| Amylene-vapour | 2 | ................ | 4·8530 |
| | 1 | ................ | 2·4265 |

The vapour is rapidly and completely absorbed by anhydrous sulphuric acid and by pentachloride of antimony. (Frankland.)

[The most volatile portion of the oily mixture, which, according to Cahours, is deposited under strong pressure (x, 411) from the illuminating gas obtained from resin, perhaps belongs to this head. This most volatile oil, *Tétraçarbure quadrihydrique* of Couerbe, is, according to that chemist, colourless, does not solidify at — 15°, boils between 28 and 30°, and has a vapour-density of 2·00. The boiling point, calculated according to Gerhardt's law, is 30°, and therefore agrees with that of Couerbe's product better than with that of Balard's; but the vapour-density of Couerbe's product differs considerably from that above calculated.]

## ¶. Amyl.

$$C^{10}H^{11} \text{ or } C^{20}H^{22} = \left.\begin{matrix} C^{10}H^{11} \\ C^{10}H^{11} \end{matrix}\right\}$$

FRANKLAND. *Chem. Soc. Qu. J.* 3, 30. *Ann. Pharm.* 74, 41.
A. WURTZ. *N. Ann. Chim. Phys.* 44, 275; *Ann. Pharm.* 96, 367.

*Formation and Preparation.* 1. By the action of zinc-amalgam on iodide of amyl. The less volatile portion of the distillate thereby obtained consists chiefly of amyl (p. 1). This liquid was not acted upon by potassium. On rectifying it, the boiling point rose rapidly to 155°, at which point it remained stationary till nearly the whole had passed over. The liquid which distilled at that temperature was collected apart. (Frankland.) — 2. By the action of sodium on iodide of amyl. No decomposition takes place in the cold, but, on the application of heat, the sodium acts upon the iodide of amyl in the same manner as upon iodide of butyl (x, 563). The liquid separated from the resulting iodide of sodium by distillation in the oil-bath is rectified, the portion which passes over at 158° being collected apart. (Wurtz.) — 3. By the electrolysis of caproic acid:

$$C^{12}H^{12}O^4 = C^{10}H^{11} + 2CO^2 + H.$$

A concentrated solution of caproate of potash is subjected to the action of a zinc-carbon battery of six elements in the apparatus used by Kolbe for the electrolysis of acetate of potash (vii, 247). The liquid soon becomes turbid, and oily drops collect on the surface. This oil is removed by a pipette, and distilled with an alcoholic solution of potash, then washed with water, dried, and rectified. The product thus obtained is amyl. The potash retained caproic [?] acid. (Brazier and Gossleth, *Chem. Soc. Qu. J.* 3, 222.)

*Properties.* Transparent, colourless liquid having a slight ethereal odour and a burning taste. (Frankland.) Colourless, mobile liquid having an aromatic odour. Turns the plane of polarisation to the right; but preparations obtained with iodide of amyl produced from different samples of amylic alcohol possess this power in different degrees. (Wurtz.) Sp. gr. = 0·7704 at 11° (Frankland); 0·7413 at 0°, and 0·7282 at 20°. (Wurtz.) At 30° it becomes thick and oily, but does not solidify. (Frankland). — Boils at 155° under a pressure of 728mm. (Frankland); at 158° (Wurtz); at 155°. (Brazier and Gossleth.) Vapour-density = 4·90 (Frankland); 4·956. (Wurtz).

| | | | Frankland. | Wurtz. | Braz. & Goss. |
|---|---|---|---|---|---|
| 10 C | 60 | 84·5 | 84·3 | 84·20 | 84·26 |
| 11 H | 11 | 15·5 | 15·3 | 15·65 | 15·70 |
| $C^{10}H^{11}$ | 71 | 100·0 | 99·6 | 99·85 | 99·96 |

| | Vol. | Density. | Or: Vol. | Density. |
|---|---|---|---|---|
| C-vapour | 10 | 4·1600 | 20 | 8·3200 |
| H-gas | 11 | 0·7623 | 22 | 1·5246 |
| Amyl-vapour | 1 | 4·9223 | 2 | 9·8446 |
| | | | 1 | 4·9223 |

For the controversy about the formulæ and vapour-volumes of the alcohol-radicals, see vii, 172; the double formulæ, *e. g.* $C^{20}H^{22}$ for amyl, are powerfully corroborated by Wurtz's discovery of the compound radicals, ethylo-butyl, ethylo-amyl, &c. (p. 5.)

*Decompositions.* 1. Amyl does not take fire in the air at ordinary temperatures, but on being heated, its vapour burns with a white smoky flame. (Frankland.) — 2. It is not affected by fuming sulphuric acid, and is but very slowly oxidised by boiling fuming nitric acid, or by a mixture of nitric and sulphuric acid, the liquid acquiring the odour of valerianic acid. (Frankland.) Strong nitric acid dissolves amyl when boiled with it for some time, the vapours being continually condensed and allowed to flow back again; and the solution, when neutralised with carbonate of potash and concentrated, yields a neutral yellow substance sparingly soluble in water, and ultimately solidifies to a crystalline mass of nitrate of potash, which, when treated with alcoholic potash, yields a small quantity of a yellow deliquescent potash-salt; no valerianic acid could be detected among the products of the oxidation. (Wurtz.) — Amyl does not dissolve in oil of vitriol or in fuming sulphuric acid; when left for some time in contact with the latter, it blackens and ultimately gives off sulphurous acid. When the vapour of anhydrous sulphuric acid is passed into amyl cooled by a freezing mixture, the liquid slowly blackens, and gives off sulphurous acid: but no conjugated sulphuric acid is produced. — 3. Hydriodic and hydrochloric acid do not act upon amyl even at 300°. — 4. Pentachloride of phosphorus does not act upon amyl at ordinary temperatures; on the application of heat, it dissolves and separates out with scarcely any alteration on cooling; after long boiling, however, the amyl is decomposed, with evolution of hydrochloric acid and terchloride of phosphorus, and formation of substitution-products. When 7 pts. (1 At.) amyl were boiled with 21 pts. (2 At.) pentachloride of phosphorus, till the liquid began to show colour, the residue then washed with water, dried over chloride of calcium and distilled, the thermometer quickly rose to 210°; between 210° and 215° a distillate passed over containing 58·26 p. c. C and 10·61 H; and between 215° and 220°, another distillate containing 57·04 p. c. and 9·80 H, agreeing nearly with the formula $C^{10}H^{10}Cl$ or $C^{20}H^{20}Cl^2$ which requires 56·92C and 9·48 H. Equation for the formation of this product:

$$C^{10}H^{11} + PCl^5 = C^{10}H^{10}Cl + PCl^3 + HCl.$$

When 5 pts. of amyl were boiled for several days with 30 pts. of the pentachloride (1 At. to 4 At.), the less volatile vapours being condensed and made to flow back, the pentachloride of phosphorus gradually disappeared, with formation of hydrochloric acid and terchloride of phosphorus; as soon as the liquid began to show colour, the boiling was stopped, and the product washed, dried and distilled. The distillate obtained above 270°, was a colourless neutral liquid, heavier than water, insoluble in water, but soluble in alcohol; it contained 41·80 p. c. C and 6·86 H, agreeing nearly with the formula $C^{10}H^9Cl^2$ or $C^{20}H^{18}Cl^4$ which requires 48·25 C and 6·42 H. When this liquid was heated in a sealed tube with alcoholic potash, it yielded chloride of potassium, and, after addition of water, an oily liquid separated out, which distilled at about 220°, but without exhibiting a constant boiling point. (Wurtz.) — 5. Pentachloride of antimony acts upon amyl with evolution of hydrochloric acid and formation of substitution products. — 6. Chloride of mercury heated with amyl is reduced at about 250°, with evolution of hydrochloric acid; but no chloride of amyl is formed. (Wurtz.)

*Combinations.* Amyl unites, though not directly, with oxygen, chlorine, iodine, &c., forming a series of compounds homologous with

the ethyl-compounds. Also with hydrogen, with various metals, *e. g.* zinc, tin, &c., and with other organic radicals, such as ethyl and butyl.

It is insoluble in water, but mixes in all proportions with alcohol and ether. (Frankland.)

*Ethamyl.* $C^{14}H^{16} = \left.\begin{matrix} C^4H^5 \\ C^{10}H^{11} \end{matrix}\right\}$ — *Preparation.* 70 grm. iodide of amyl and 60 grm. iodide of ethyl were decomposed with sodium; and in another operation, 34 grm. iodide of amyl and 27 grm. iodide of ethyl with 8 grm. of sodium. When the action was nearly at an end, 50 grm. iodide of amyl, 40 grm. iodide of ethyl, and 12 grm. sodium were added to the product, and the heating continued; altogether 154 grm. iodide of amyl and 127 grm. iodide of ethyl were decomposed with 34 grm. sodium; but these materials were divided as above, in order that the action might not become too violent. When the decomposition was ended, the product was distilled in the oil-bath, the portion which went over below 120° being collected apart, and this distillate was heated under a sealed glass tube with excess of sodium, to complete the decomposition of any organic iodine-compounds that might still be present. The liquid was then again distilled; and the distillate submitted to repeated fractional rectification, yielded ethamyl in the form of a liquid which passed over between 87·5 and 89·5, and for the most part at 88°.

Ethamyl has a sp. gr. of 0·7069 at 0°; boils at 88°. Vapour-density 3·523. It turns the plane of polarization to the right. It is but slightly attacked by pentachloride of phosphorus at its boiling point (88°); but when the two substances are heated together in a sealed glass tube above 100°, a more violent action takes place; the products could not however be examined because the tube exploded. (Wurtz, *Ann. Pharm.* 95, 370.)

| | | | Wurtz. |
|---|---|---|---|
| 14 C | 84 | 84 | 84·02 |
| 16 H | 16 | 16 | 16·14 |
| $C^{14}H^{16}$ | 100 | 100 | 100·16 |

| | Vol. | Density. |
|---|---|---|
| C-vapour | 14 | 5·8240 |
| H-gas | 16 | 1·1088 |
| Vapour of Ethamyl | 2 | 6·9328 |
| | 1 | 3·4664 |

*Butamyl.* $C^{18}H^{20} = \left.\begin{matrix} C^8H^9 \\ C^{10}H^{11} \end{matrix}\right\}$ — 160 grms. of a mixture of iodide of butyl and iodide of amyl were decomposed by 20 grm. sodium. On distilling the product, the greater portion passed over between 130° and 140°; and by repeated fractional distillation, the butamyl was obtained in the form of a liquid which had a sp. gr. of 0·7247 at 0°, boiled at 132°, and exhibited a vapour-density = 4·465. (Wurtz.)

| | | | Wurtz. |
|---|---|---|---|
| 18 C | 108 | 84·37 | 84·38 |
| 20 H | 20 | 15·63 | 15·77 |
| $C^{18}H^{20}$ | 128 | 100·00 | 100·15 |

| | Vol. | Density. |
|---|---|---|
| C-vapour | 18 | 7·4880 |
| H-gas | 20 | 1·3860 |
| Vap. of Butamyl | 2 | 8·8740 |
| | 1 | 4·4370 ¶. |

## Hydride of Amyl.

$$C^{16}H^{12} = C^{10}H^{10},H^2 = C^{10}H^{11},H.$$

FRANKLAND (1850). *Ann. Pharm.* 74, 41.

*Amyl-hydrogen, Amyl-wasserstoff, Lemyle.*—Constitutes, perhaps, the most volatile portion of eupione, and probably exists also in coal-gas.

*Formation and Preparation.* 1. The mixture of amyl and hydride of amyl (p. 2) which distils over at 80° is placed in contact at −10°, for several hours, with oil of vitriol saturated with anhydrous sulphuric acid, and frequently agitated, whereupon a stratum of liquid rises to the surface about equal in volume to the mixture employed. The product is then distilled in the water-bath at a gentle heat, whereupon the hydride of amyl passes over, whilst the upper liquid is reduced to a layer half as deep, and consisting probably of a conjugated compound of amylene with sulphuric acid; lastly, the distillate is freed from admixed sulphurous acid by contact with sticks of fused hydrate of potash.—2. More conveniently: Iodide of amyl is heated with water and with zinc to 142° in a long glass tube drawn out to a point at the open end; the mixture left to cool after the action is completed; the point of the tube broken off; the open end connected by means of a cork with a distillation-tube; and the liquid distilled at 60°, the distillate placed for 24 hours in contact with hydrate of potash, and rectified in the water-bath at 35°.

*Properties.* Transparent, colourless, very mobile liquid, which does not solidify at 24°; has a density of 0·6385 at 14°; boils at 30° when the barometer stands at 0·758 met. and exhibits a vapour-density of 2·4657 to 2·4998. Has a pleasant odour like that of chloroform.

| | | | | | | Frankland. |
|---|---|---|---|---|---|---|
| 10 C | 60 | .... | 83·33 | .... | | 83·33 |
| 12 H | 12 | .... | 16·67 | .... | | 16·62 |
| $C^{10}H^{12}$ | 72 | .... | 100·00 | .... | | 99·95 |

| | Vol. | | Density. |
|---|---|---|---|
| C-vapour | 10 | .... | 4·1600 |
| H-gas | 12 | .... | 0·8316 |
| Vap. of $C^{10}H^{12}$ | 2 | .... | 4·9916 |
| | 1 | .... | 2·4958 |

[That this compound is $C^{10}H^{12}$, and not as supposed by Frankland, $C^5H^6$, follows rom its vapour-density, and from its boiling-point; the latter is indeed higher than it should be for $C^{10}H^{12}$, according to Gerhardt's law. (vii, 57.) Similar observations apply to the compound described by Frankland and Kolbe (*Ann. Pharm.* 65, 270), as methyl, $C^2H^3$, which should really be regarded as $C^4H^6$, and stands to ethylene $C^4H^4$, in the same relation as marsh-gas $C^2H^4$ to methylene $C^2H^2$; similarly for the compound described by the same chemists as ethyl, $C^4H^5$, which should be regarded as $C^8H^{10}$; also the valyl of Kolbe, $C^8H^9$, in which, for similar reasons, the atomic weight should be doubled, so that the so-called radicals are actually compounds of a nucleus with 2 At. H.—Compare vii. 172.]

*Decompositions.* Hydride of amyl burns with a white, very luminous flame. It is but slowly attacked by the strongest oxidising agents, and by fuming oil of vitriol not at all.

*Combinations.* It is insoluble in water. It dissolves readily in *alcohol* and *ether*, being separated from the former by water. (Frankland.) ¶.

## Oxide of Amyl, or Amylic Ether.

$$C^{10}H^{11}O = C^{10}H^{10},HO.$$

BALARD. (1844.) *N. Ann. Chim. Phys.* 12, 299.

*Amyloxyd, Myläther, Ether amylique.*

*Formation and Preparation.* Chloride of amyl mixed with alcoholic potash in a strong sealed tube and heated to 100°, yields amylic ether and a deposit of chloride of potassium. (Balard.) This product was most probably vinamylic ether, (p. 8.) — Gaultier (*Compt. rend.* 15,171) states that by distilling fusel-oil with oil of vitriol, he obtained amylic ether, among other products, as a colourless, agreeably smelling liquid, which dissolved with red colour in oil of vitriol, but boiled at 170° [certainly too high for amylic ether]. A similar liquid was obtained in the same manner by Rieckher. See also Williamson (p. 8).

*Properties.* Colourless liquid boiling at 111° to 112° and having an agreeable odour. (Balard.)

| | | | Williamson. |
|---|---|---|---|
| 10 C | 60 | 75·95 | 75·81 |
| 11 H | 11 | 13·92 | 14·09 |
| O | 8 | 10·13 | 10·10 |
| $C^{10}H^{11}O$ | 79 | 100·00 | 100·00 |

*Decomposition.* The ether prepared by Balard's method is converted, when treated with chlorine-gas under the influence of heat and sunshine, till the chlorine no longer appears to act, into a product which may be regarded as a mixture of bi-, quinti-, and sexti-chlorinated amylic ether with chloraldehyde and sesquichloride of carbon. For:

$$2C^{10}Cl^{11}O + 6Cl = C^4Cl^4O^2 + 4C^4Cl^6.$$

The product gives up to water, terchloracetic acid produced from the chloraldehyde (ix, 209); the rest of the product, heated with alcoholic potash deposits a large quantity of chloride of potassium, and afterwards, on dilution with water, a brown, neutral, oily, chlorinated mixture of several substances, while valerate, terchlorovalerate and quadrichlorovalerate of potash remain dissolved. The bichlorinated amylic ether acted upon by potash, yields in fact valerate of potash:

$$C^{10}Cl^2H^9O + 3KO = C^{10}H^9KO^4 + 2KCl;$$

the quintichlorinated ether yields terchlorovalerate of potash:

$$C^{10}Cl^5H^6O + 3KO = C^{10}Cl^3H^6KO^4 + 2KCl;$$

and the sextichlorinated ether yields quadrichlorovalerate of potash:

$$C^{10}Cl^6H^5O + 3KO = C^{10}Cl^4H^5KO^4 + 2KCl.$$

The dark colour of the separated neutral oil is due to the brown substance produced by the action of the excess of potash on the chlorovalerianic acid. (Malaguti, *N. Ann. Chim. Phys.* 27, 417.)

## ¶. Methamylic Ether.

$$C^{12}H^{14}O^2 = C^2H^3O,C^{10}H^{11}O = \left.\begin{matrix}C^2H^3\\C^{10}H^{11}\end{matrix}\right\} O^2.$$

A. W. Williamson. *Chem. Soc. Qu. J.* 4, 108, 234.

*Methylate of Amyl, Amylate of Methyl.*

*Formation and Preparation.* 1. By the action of iodide of methyl on amylate of sodium $C^{10}H^{11}KO^2$, or of iodide of amyl on methylate of sodium, $C^2H^3KO^2$,

$$\text{Or: } \left.\begin{matrix}C^{10}H^{11}KO^2 + C^2H^3I\\C^2H^3KO^2 + C^{10}H^{11}I\end{matrix}\right\} = KI + C^{12}H^{14}O^2$$

It is purified in the same manner as vinomethylic ether (viii, 193).—. 2. By the action of oil of vitriol on a mixture of 1 At. methylic and 1 At. amylic alcohol, the process being conducted as in the continuous method of preparing common ether (viii, 173). The product is a mixture of methamylic ether with methylic ether, amylic ether, and excess of the two alcohols, which may be removed by distillation over hydrate of potash. The methamylic ether is then purified by fractional distillation, which is easily effected, in consequence of the great difference of the boiling points of the three ethers.

*Properties.* Transparent, colourless liquid, which boils at 92°, and has a vapour-density of 3·74.

| | | | Williamson. |
|---|---|---|---|
| 12 C | 72 | 70·59 | 70·24 |
| 14 H | 14 | 13·72 | 13·87 |
| 2 O | 16 | 15·69 | 15·89 |
| $C^{12}H^{14}O^2$ | 102 | 100·00 | 100·00 |

| | Vol. | Density. |
|---|---|---|
| C-vapour | 12 | 4·9920 |
| H-gas | 14 | 0·9702 |
| O-gas | 1 | 1·1093 |
| Vap. of $C^{12}H^{14}O^2$ | 2 | 7·0715 |
| | 1 | 3·5357 |

The ether analysed was prepared by the first process.

## ¶. Vinamylic Ether.

$$C^{14}H^{16}O^2 = C^4H^5O,C^{10}H^{11}O = \left.\begin{matrix}C^4H^5\\C^{10}H^{11}\end{matrix}\right\} O^2.$$

Williamson. *Chem. Soc. Qu. J.* 4, 108, 234.

*Formation and Preparation.* Exactly similar to that of methamylic ether.

*Properties.* Transparent, colourless liquid, boiling at 112°. Vapour-density 4·042.

| | | | Williamson. a. | Williamson. b. |
|---|---|---|---|---|
| 14 C | 84 | 72·41 | 72·42 | 72·46 |
| 16 H | 16 | 13·79 | 13·99 | 13·73 |
| 2 O | 16 | 13·80 | 13 59 | 13·81 |
| $C^{14}H^{16}O^2$ | 116 | 100·00 | 100,00 | 100·00 |

| | Vol. | Density. |
|---|---|---|
| C-vapour | 14 | 5·8240 |
| H-gas | 16 | 1·1088 |
| O-gas | 1 | 1·1093 |
| Vap. of $C^{14}H^{16}O^2$ | 2 | 8·0421 |
| | 1 | 4·0210 |

*a* was prepared by the action of iodide of ethyl on amylic alcohol; *b*, by the action of oil of vitriol on a mixture of vinic and amylic alcohols.

The product which Balard obtained by the action of alcoholic potash on chloride of amyl, and supposed to be amylic ether, was probably vinamylic ether. (Williamson.) ¶.

## Amylic Alcohol.

$$C^{10}H^{12}O^2 = C^{10}H^{10}, H^2O^2.$$

GABRIEL PELLETAN. *J. Chim. med.* 1, 76; also *Ann. Chim. Phys.* 30, 221; also *N. pr.* 1, 135.

DUMAS. *Ann. Chim. Phys.* 56, 314; also *J. Chim. med.* 10, 705; also *Pogg.* 34, 335; also *Ann. Pharm.* 13, 80; also *J. pr. Chem.* 3, 321.

DUMAS & STAS. *Ann. Chim. Phys.* 73, 128; also *Ann. Pharm*, 35, 143; also *J. pr. Chem.* 21, 278.

CAHOURS. *Ann. Chim. Phys.* 70, 81; also *Ann Pharm.* 30, 288; also *J. pr. Chem.* 17, 213.—*Ann. Chim. Phys.* 75, 193; also *Ann. Pharm.* 37, 164; also *J. pr. Chem.* 22, 171.

APJOHN. *Phil. Mag. J.* 17, 86.

BALARD. *N. Ann. Chim. Phys.* 12, 294; also *J. pr. Chem.* 34, 123; abstr. *Compt. rend.* 19, 634; abstr. *Ann. Pharm.* 42, 311.

RIECKHER. *Jahrb. pr. Pharm.* 14, 1.

PASTEUR. *Compt. rend.* 41, 296; *Ann. Pharm.* 96, 255; *Chem. Soc. Qu. J.* 8, 277.

*Amylalkohol, Hydrated Oxide of Amyl, Hydrate of Amyl, Potato Fusel-oil, Corn Fusel-oil; Mylalkohol, Kartoffelfuselöl, Fuselöl, Amylal, Amyloxyd-hydrat, Huile de pomme de terre, Hydrate d'Oxyde d'Amyle, Alcool amylique.*—Known since Scheele (*Crell. Ann.* 1785, 1, 61); more exactly investigated chiefly by Pelletan, Dumas, Cahours, and Balard.

*Sources.* In brandy from potatoes, barley, rye, beet-molasses, grape-husks and wine lees, often mixed with margaric acid and œnanthic ether. Fusel-oil is contained, not only in ordinary potato-brandy, but also, according to Dubrunfaut, in that which is obtained by converting potato-starch into grape-sugar by means of sulphuric acid, and fermenting the sugar. Barley-brandy yields by rectification, nothing but potato fusel-oil, without any of the substances which Mulder & Kolbe (*vid. inf.*)

found in rye-brandy. (Medlock, *Ann. Pharm.* 69, 214.)—Wort prepared from malt which has been roasted with peat-smoke, as it is done in Scotland, yields, when made to undergo the vinous fermentation and distilled, a spirit (whisky) which contains fusel-oil. Wort from unmalted barley yields, after fermentation, a spirit much richer in fusel-oil. But if the wort, before fermentation, be boiled with hops, the spirit obtained from it is free from fusel-oil. (Glassford, *Ann. Pharm.* 54, 104.) — In the rectification of brandy prepared from rye, the distillate obtained after the greater part of the alcohol has passed over, is turbid and contains fusel-oil. This distillate when cooled deposits a tallowy substance, of the nature of fusel-oil. (Scheele, *Opusc.* 2, 275.) It deposits on the flannel in the funnel of the receiver, a salve-like substance having the odour of fusel-oil. (Gehlen, *Schw.* 1, 277.) The milky liquid, which, in the rectification of corn-brandy, passes over after the alcohol, leaves when filtered, a soft solid mass coloured green by oxide of copper, and from which, even at ordinary temperatures, delicate white needles sublime in the vessels in which it is kept. (Gm.) This substance, which was more particularly examined by Gehlin, was designated by the author (*Handbuch*, Aufl. 3, ii, 421) as *fusel-camphor*. But, according to recent investigations, it is a mixture of potato fusel-oil with margaric acid, œnanthic ether or œnanthic acid, and corn-oil. According to Kolbe (*Ann. Pharm.* 41, 53), the dark brown, greasy mass, smelling strongly of fusel-oil, which collects in the receiver during the distillation of corn-brandy, contains, besides fusel-oil, a very large quantity of margaric acid, a small quantity of œnanthic acid, and from 1 to 2 p. c. of corn-oil. Mulder (*Pogg.* 41, 582) found, in a dark brown, disagreeably smelling oil obtained in the rectification of corn-brandy, which had a greenish yellow colour after rectification, nothing but œnanthic ether, and the substance which he calls *corn-oil, Oleum siticum*, which is greenish yellow and smells like *Phellandrium*. [Since, however, it was obtained by distilling the entire oil with potash-ley, whereupon œnanthate of potash remained and alcohol passed over with the corn-oil, and since the corn-oil which Mulder obtained with dilute potash was = $C^{42}H^{35}O^4$, while that which was obtained with concentrated potash = $C^{24}H^{17}O$, it appears that all kinds of decomposition-products were formed]. Mulder afterwards found (*Ann. Pharm.* 45, 67; also *J. pr. Chem.* 32, 219), in some kinds of corn fusel-oil, a large quantity of margaric acid, but in others a small quantity, and in others again, none at all. Medlock (*Ann. Pharm.* 69, 214) obtained by the rectification of rye-brandy, nothing but potato fusel-oil. A volatile oil from corn-brandy is described by Buchner. (*Repert*, 24, 270.) The brandy obtained from *beet-molasses* which has undergone the vinous fermentation, yields an oil, which after sufficient purification, agrees perfectly with potato fusel-oil. (Gaultier de Claubry, *Compt. rend.* 15, 171; also *Ann. Pharm.* 44, 127; also *J. pr. Chem.* 27, 56.) In the rectification of brandy obtained from grape-skins after the wine has been expressed (*Weintresterbranntwein*), there passes over, after the pure alcohol, a spirit containing fusel-oil, and afterwards a watery liquid turbid from the presence of oil. On mixing these last two distillates together, adding water, and leaving the mixture at rest, the wine fusel-oil rises to the surface, in the form of a thin colourless liquid which soon acquires a yellowish tint, cannot be distilled without decomposition, has a pungent odour, and intolerably sharp taste; a single drop of this liquid is sufficient to impart a disagreeable flavour to a litre of alcohol. (Ambergier, *Ann. Chim. Phys.* 14, 210.) This wine fusel-oil is a mixture of a

large quantity of œnanthic ether with potato fusel-oil and a little alcohol; and it is chiefly the œnanthic ether contained in it, which imparts to the alcohol the disagreeable taste of grape-skin brandy. (Balard, *N. Ann. Chim. Phys.* 12, 294 and 327.) The wine fusel-oil obtained by the distillation of *Jena wine-lees* is thickish; deposits at $-4°$, a large quantity of camphor-like matter; has a density of 0·856; is yellowish brown, but soon becomes dark brown; has a not very unpleasant odour, but an excessively repulsive taste, and excites a persistent and violent irritation in the mouth and throat; in the fresh state it does not redden litmus, but after keeping for a year, reddens it strongly. The spots which it makes upon paper do not disappear till they have been heated for some time. It burns with a dark yellowish red flame, and acquires a dark carmine colour by contact with oil of vitriol, &c. (Stickel, *N. Br. Arch.* 9, 22; compare also Buchner, *Repert.* 58, 86.)

It is highly probable that fusel-oil does not exist ready formed in potatoes, corn, grapes, &c. but is produced by fermentation. — Payen supposes the fusel-oil to pre-exist in potatoes, because he was able to extract an oil from potato-starch by treating it with alcohol, and because, in converting potato-starch into sugar by boiling it in a still with water containing sulphuric acid, he obtained an oil smelling of starch, and amounting to 0·001 of the starch; this oil was however more volatile than fusel-oil. But, according to Bucholz, the oil extracted by alcohol from potatoes, is buttery, and without the taste or smell of fusel-oil; similar observations apply to that which is obtained from rye. Schrader and Körte (*Schw.* 1, 273) suppose that the fusel-oil is produced from fatty matter of this kind, when the fermentation is badly conducted and the product too quickly distilled. According to Liebig's suggestion (*Chem. Briefe,* 165), fusel-oil is produced by partial decomposition of common alcohol :

$$5C^4H^6O^2 = 2C^{10}H^{12}O^2 + 6HO;$$

and, according to Dumas & Balard, by a decomposition of grape-sugar induced by excess of ferment [according to what equation ?].— ¶ Chancel (*Compt. rend.* 37, 410,) supposes that amylic and propylic alcohol are produced together by the decomposition of grape sugar, according to the equation :

$$2C^{12}H^{12}O^{12} = C^6H^8O^2 + C^{10}H^{12}O^2 + 8CO^2 + 4HO;$$

(*vid.* ix, 399); but propylic alcohol does not appear to be always contained in fusel-oil (*comp.* Würtz, *Ann. Pharm.* 93, 110) ¶. Finally, according to the supposition of Deschamps (*N. Ann. Chim. Phys.* 12, 383), wine fusel-oil is produced only from the skins of the grapes by fermentation and subsequent heating to 100°.

*Preparation.* In the rectification of *potato* or *corn brandy*, the fusel-oil being less volatile remains behind for the most part, passing over in considerable quantity, together with water, only with the last portions of the spirit, and separating out on the surface of the liquid when a larger quantity of water is added. Crude fusel-oil, which may be obtained in abundance from the large brandy distilleries, is yellow, reddish yellow or red-brown, of sp. gr. 0·84 to 0·93, and still retains alcohol and water. It is freed from alcohol by washing with water, and then from water by rectification over chloride of calcium. (Pelletan.) A small quantity of alcohol remains with it. (Dumas).—The oil is shaken up with an equal quantity of water; then distilled after being separated from the water by treating

with an equal quantity of pounded chloride of calcium; the receiver changed as soon as the boiling point reaches 131°, at which point it remains steady till the end of the distillation; and the latter distillate rectified, rejecting the portion which goes over last. The fusel-oil obtained below 131° still retains alcohol. (Apjohn, *Phil. Mag.* 17, 86.) — The oil freed from the greater part of the alcohol by repeated agitation with water, is rectified; the receiver changed as soon as the boiling point rises to 132°, at which point it then remains constant during the whole distillation; and this distillate repeatedly rectified. (Cahours.) — A similar process is followed by Kopp (*Ann. Pharm.* 55, 196), according to whom, however, the boiling point slowly rises above 132°; he examined the liquid which passed over at 134°. — According to Krutzsche (*J. pr. Chem.* 31, 1,) the boiling point of the crude oil washed with water, remains stationary for some time at 132°, and then gradually rises above 160° [probably from admixture of margaric acid or œnanthic ether]. But the distillate obtained between 132° and 135°, yields after repeated rectification an oil boiling at 132°. — The crude oil is distilled without any preparatory treatment, whereupon a mixture of oil, water, and common alcohol passes over; and the portion which distils over between 130° and 132°, is purified by repeated rectification. (Dumas, Medlock, Rieckher.)

2. To obtain pure fusel-oil from the oil of *grape-skin brandy*, this oil is distilled; the portion which goes over between 130° and 140° collected apart, and re-distilled after addition of hydrate of potash, whereby the admixed œnanthic ether is decomposed and the œnanthic acid retained; and the receiver changed, as soon as the boiling point has risen to 132°: the fusel-oil thus obtained is very pure. (Balard.)

¶ *Active and Inactive Amylic Alcohol.* — The fusel-oil of commerce consists chiefly of a mixture of two kinds of amylic alcohol,—one active, and the other inactive with regard to polarised light. These two varieties are exactly similar in their chemical properties; differ but slightly in density and boiling point; and give rise, under similar circumstances, to products which resemble each other in all respects, excepting in their relation to polarised light, those which are derived from the active alcohol being themselves active, and those which result from the inactive alcohol being themselves also inactive. — The proportion of the active and inactive alcohols in fusel-oil varies according to its origin; thus the fusel-oil obtained by fermentation of the juice of mangold-wurzel contains about one-third of active, and two-thirds of inactive amylic alcohol, whereas that which is produced by fermentation of the molasses contains about equal parts of the active and inactive alcohols. The two alcohols cannot be separated by fractional distillation, but only by fractional crystallisation of the active and inactive sulphamylates of baryta. For this purpose it is necessary to prepare a large quantity of sulphamylate of baryta from crude amylic alcohol rectified by a single distillation, in order to free it from water and vinic alcohol. The amylic alcohol thus far purified is mixed, as usual, with an equal weight of sulphuric acid, the mixture treated with carbonate of baryta, then filtered and left to crystallise. The crystals have all the same aspect, lustre, form, and angles; and, as in the case of a perfectly constant and homogeneous substance, the salt may be crystallised either wholly or partially any number of times, without the slightest change in the aspect of the crystals. Nevertheless the mass is really composed of two kinds of crystals differing in

solubility, and in their action on polarised light,—one being, indeed, active, and the other inactive. They are very difficult to separate, in consequence of their complete isomorphism. Nevertheless, the active salt is $2\frac{1}{2}$ times more soluble than the inactive; and if the first crystals which separate be recrystallised about 20 times, a product is at length obtained which has no action on polarised light; and by repeatedly crystallising the mother-liquor, a solution is ultimately left containing nothing but the active salt. Lastly, on extracting from these two varieties of the sulphamylate, the amylic alcohol of which they contain the elements, it is found that the more soluble salt yields an amylic alcohol which rotates the plane of polarisation to the left, and to the amount of 20° in a tube 50 centimetres long, while the less soluble salt yields an amylic alcohol which has no perceptible action on polarised light. (Pasteur, *Compt. rend.* 41, 296) ¶.

*Properties.* Transparent, colourless, thin oily liquid, greasy to the touch. (Pelletan.) Solidifies at — 19° to — 20°, forming a crystalline, laminated mass, and melts again at — 18°. (Pelletan.) Does not solidify at — 21° (Apjohn); requires for its solidification a temperature of — 23° or still lower. (Pierre.) Sp. gr. : 0·82705 at 0° (Pierre, *N. Ann. Chim. Phys.* 19, 197); 0·8253 at 0° and 0·8137 at 15° (Kopp); or, according to a later determination by Kopp, (*Ann Pharm.* 94, 290), 0·8248 at 0°, and 0·8113 at 18·7°; 0·8138 (Apjohn); 0·8184 at 15° (Cahours); 0·8185 at 13° (Rieckher); 0·821 at 16° (Pelletan); 0·818 at 14° (Delffs, *N. Jahrb. Pharm.* 1, 1); Index of refraction for the red ray, 1·3601 (Delffs). — Boiling point: 125° at 0·76 met. atmospheric pressure (Pelletan) [too low in consequence of the presence of common alcohol]; 131° (Apjohn); 131·5° (Dumas); 131·8 at 0·751 met. (Pierre); 132° at 0·76 met. (Cahours); 133° at 27″ 9‴ and with platinum-wire immersed (Kopp); in a later experiment (*Ann. Pharm.* 94, 289) Kopp found that a thermometer with its bulb immersed in the liquid showed, at the commencement of the ebullition, a temperature of 129·6°, and afterwards slowly rose; while a thermometer with its bulb in the vapour marked 130·9° at first and slowly rose to 131·6°, (these temperatures determined by Kopp, are corrected for the difference of temperature of the mercury in the tube and bulb); 134° (Rieckher); 132° at 339·7 Par. lines. (Delffs.) The active alcohol boils at 127° to 128°, under the ordinary pressure, and the inactive alcohol at 129°. The mixture of the two boils at intermediate temperatures. (Pasteur.) — Specific heat 0·5873. Latent heat of vapour 121·37. (Favre and Silbermann, *N. Ann. Chim. Phys.* 37, 461.) — Vapour-density : 3·137 (Apjohn); 3·147 (Dumas); 3·20 (Balard). The oil makes a transient grease-spot upon paper. (Pelletan.) Its odour is penetrating (Pelletan), repulsive (Dumas), peculiarly pungent (Apjohn); in the pure state it has a less disagreeable odour than when diluted. (Rieckher.) Its taste is persistently sharp and warm (Pelletan, Cahours); sharply bitter, somewhat like that of oil of cloves. (Apjohn.) The vapour when inhaled, or a drop of the liquid placed on the tongue, excites, in susceptible persons, coughing, nausea, giddiness, and fainting, and especially weakens the lower extremities, even for 24 hours. In dogs, a few table-spoonsful merely produce vomiting; in rabbits, two tea-spoonsful excite vomiting, and larger doses produce oppression of the chest and death; still smaller animals are rendered insensible by a few drops, and asphyxiated and killed, with convulsions and interrupted respiration. Ammonia acts as an antidote. (Pelletan.) According to

Schlossberger (*Ann. Pharm.* 73, 212), amylic alcohol acts upon the animal organism like vinic alcohol, being quickly decomposed in the blood, producing intoxication and death-like sleep, and acting in the same manner on the mucous membranes. — Amylic alcohol is neutral.

| | | | Dumas. | Cahours. | Apjohn. | Balard. | Kopp. | Pierre. |
|---|---|---|---|---|---|---|---|---|
| 10 C | 60 | 68·18 | 68·95 | 68·51 | 68·13 | 67·65 | 67·68 | 68·00 |
| 12 H | 12 | 13·64 | 13·60 | 13·52 | 13·33 | 13·75 | 13·67 | 13·87 |
| 2 O | 16 | 18·18 | 17·45 | 17·97 | 18·54 | 18·60 | 18·65 | 18·13 |
| $C^{10}H^{12}O^2$ | 88 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 |

| | Vol. | Density. |
|---|---|---|
| C-vapour | 10 | 4·1600 |
| H-gas | 12 | 0·8316 |
| O-gas | 1 | 1·1093 |
| Vapour of Amylic Alcohol | 2 | 6·1009 |
| | 1 | 3·0504 |

*Decompositions.* ¶. 1. Amylic alcohol passed in the state of vapour through a long glass-tube at a moderate red heat, is resolved into propylene gas and marsh gas in about equal volumes; a liquid also condenses which appears to be unaltered amylic alcohol. If the heat be too low, but little gas is formed; if it be too great, scarcely anything but marsh-gas is obtained. (Reynolds, *Chem. Soc. Qu. J*, 3, 111; compare ix, 395.) ¶ — 2. Fusel-oil is difficult to *set on fire,* and burns with a white luminous flame, leaving a small glutinous residue (Pelletan); burns with a pure blue flame (Cahours); with a bright smoky flame. (Apjohn.) — 3. It is not much altered by being kept for two years in bottles containing air, but acquires the power of reddening litmus slightly, in consequence of the formation of a volatile oily acid [valerianic acid?] (Cahours.) — 4. When fusel-oil burns in the *glow lamp* (ii, 56), a liquid condenses, which forms with potash a substance resembling the resin of aldehyde, but does not reduce silver-salts, or yield any crystalline product with ammonia. (Balard.) When heated platinum-black is moistened with fusel-oil, and covered with a glass bell-jar open at top and standing in a plate containing water, valerianic acid soon begins to run down the sides of the bell-jar into the plate. (Cahours.)

$$C^{10}H^{12}O^2 + O^4 = C^{10}H^{10}O^4 + 2HO.$$

This transformation likewise takes place in vinegar manufactories, when brandy containing fusel-oil is used, so that sometimes the odour of valerianic acid is perceptible, only however at temperatures above 36°, while, below that point, any fusel-oil that may be present is converted into acetate of amyl, which has not an unpleasant odour. (Döbereiner.) Fusel-oil may also be converted into valerianic acid by passing a stream of oxygen through it at a boiling heat, the apparatus being so arranged that the vapours which rise may be condensed and flow back again. (R. Railton, *Chem. Soc. Qu. J.* 6, 209.)

5. When *chlorine gas* is passed for several hours through fusel-oil, the gas is abundantly absorbed, with great rise of temperature and evolution of hydrochloric acid, and the fusel-oil is converted into a compound resembling chloral. (Cahours.) —6. When a solution of fusel-oil in a large quantity of water containing a little potash, is treated with *bromine* or *iodine,* till those bodies are no longer decolorised, the liquid yields on evaporation a residue of valerate of potash. (Lefort, *Compt. rend.*

23, 229.) — The solution of iodine in fusel-oil turns acid from formation of hydriodic acid. (Rieckher.)

7. Strong *nitric acid* dissolves fusel-oil with violent action, the liquid turning brown as the point of saturation is attained, and then yields by distillation, not valerianic acid, but a neutral oil, probably amylic aldide. (Dumas & Stas.) — Cold nitric acid does not mix with fusel-oil or exert any action upon it; but on heating the liquid, till gas-bubbles begin to escape, decomposition takes place, which soon becomes rapid, even if the fire be quickly removed, but may be moderated by the addition of cold water. An oily mixture passes into the receiver, consisting of amylic ether, amylic aldide (inasmuch as potash forms with it a substance like aldehyde-resin, nitrate of amyl, and hydrocyanic acid; and in the retort there remains valerianic acid, probably mixed with the aldide, inasmuch as potash colours it deep brown. (Balard.) — 8. Fusel-oil is decomposed by aqueous *iodic acid*, slowly and without formation of carbonic acid. (Millon.) — 9. By aqueous *chromic acid* it is converted into valerate of amyl. — When an aqueous solution of bichromate of potash is added to a mixture of fusel-oil and strong sulphuric acid, an oil rises to the surface consisting of amylic aldide (or rather, according to Balard, of valerate of amyl which is polymeric with it). (Dumas & Stas.) — A cold-saturated aqueous solution of bichromate of potash, supersaturated with oil of vitriol, becomes heated on addition of fusel-oil, and is converted into a mixture of valerianic acid and chrome-alum, with amylic aldide floating on the surface. (Balard.) — 10. With *peroxide* of *manganese* also, a mixture of fusel-oil and strong sulphuric acid yields amylic aldide (valerate of amyl). (Dumas & Stas).

11. Fusel-oil mixes readily with *oil of vitriol*, the mixture becoming thick and acquiring a carmine colour, and, on addition of water, the fusel-oil is again separated, with pale yellow colour, but with its original odour. (Pelletan.) In this reaction, sulphamylic acid is produced and remains dissolved in the water. (Cahours.) — On distilling the solution of fusel-oil in oil of vitriol, sulphurous acid is evolved, amylene ($C^{10}N^{10}$), and its multiples ($C^{20}H^{20}$ and $C^{40}H^{40}$), pass over, together with a sulphuretted compound, and a black pitchy substance remains. (Balard.) By distillation, amylene is obtained [or chiefly rather $C^{20}H^{20}$, inasmuch as it boils at 160°], together with valerianic ether, valerianic aldide, and a liquid having an ethereal odour, and strong but not bitter taste. (Gaultier de Claubry.) — With a mixture of strong sulphuric and nitric acid, fusel-oil becomes so violently heated that the escaping vapours take fire spontaneously. (Rieckher.) — 12. Fusel-oil distilled with anhydrous phosphoric acid yields amylene and its multiples. (Balard.)

13. By *terchloride of phosphorus* added in successive portions, fusel-oil is converted, with violent evolution of heat, into phosphate of amyl, chloride of amyl, and hydrochloric acid. The latter escapes as gas together with part of the chloride of amyl:

$$3C^{10}H^{12}O^2 + PCl^3 = 2C^{10}H^{11}O,PHO^4 + C^{10}H^{11}Cl + 2HCl.$$

By addition of excess of terchloride of phosphorus, which is taken up without further rise of temperature, and then of a small quantity of water, fusel-oil is completely converted into phosphate of amyl, a portion being however further transformed, by the phosphorous acid produced at the same time, into amylophosphorous acid. (Wurtz, *N. Ann. Chim. Phys.* 16, 221.) — 14. With *pentachloride of phosphorus*, fusel-oil yields

chloride of amyl, chlorophosphoric and hydrochloric acid; (Cahours, *Compt. rend.* 22, 486; 25, 727):

$$C^{10}H^{12}O^2 + PCl^5 = C^{10}H^{11}Cl + PCl^3O^2 + HCl.$$

15. Fusel-oil absorbs *hydrochloric acid gas*, with rise of temperature and brown colouring. — 16. Fusel-oil dissolves, with the aid of heat, in aqueous *chloride of zinc*, forming a liquid which begins to boil at 130°, and yields a distillate of $C^{10}H^{10}$ and $C^{20}H^{20}$ (separable by fractional rectification at a gentle heat), which, when repeatedly distilled over chloride of zinc, are more and more converted into $C^{40}H^{40}$, perhaps by the continued action of the heat. (Balard.) With chloride of zinc, a gas is likewise attained, having the composition of ethylene. (Medlock.) — 17. By distillation with *fluoride of boron or fluoride of silicium*, amylene and its multiples are likewise obtained; on the other hand, in all these cases, no amylic ether, or but very little of it, appears to be formed. (Balard.) — 18. Fusel-oil distilled with *phosphorus and bromine*, or *iodine*, yields *bromide* or *iodide* of *amyl*.

19. Fusel-oil heated to 220° with a mixture of *hydrate of potash and lime* yields valerate of potash and hydrogen gas. (Dumas & Stas.)

$$C^{10}H^{12}O^2 + KO, HO = C^{10}H^9KO^4 + 4H.$$

The fusel-oil is heated in a retort; ten times its weight of potash-lime thrown upon it; and the mass, which spontaneously becomes warm and acquires a yellow colour by contact with the air, heated in a bath of fusible metal to 170° and then to 200°, which temperature is continued for 12 hours. At 170°, the mass turns white and begins to give off pure hydrogen gas, not mixed with any hydrocarbon, unless the heat be too suddenly raised. The residue containing the valerate of potash may be ultimately heated without residue to 230°. If, after cooling, it be exposed to the air, without being covered with water, it absorbs oxygen [and vapour of water?] with such avidity, that it burns away like tinder. (Dumas & Stas.) — ¶ 20. *Chloride of cyanogen* is rapidly absorbed by fusel-oil, and exerts upon it an action similar to that which it produces upon common alcohol (viii, 256) sal-ammoniac gradually separating out, and the liquid yielding by distillation, first, chloride of amyl, which boils at about 100°, and then amylic urethane $C^{12}NH^{13}O^4$:

$$C^{10}H^{12}O^2 + C^2NCl + 2HO = C^{12}NH^{13}O^4 + HCl.$$

[The chloride of amyl is formed by the action of the hydrochloric acid on another portion of the amylic alcohol. The formation of chloride of ammonium indicates also that of carbonate of amyl, according to the equation:

$$2C^{10}H^{12}O^2 + C^2NCl + 2HO = NH^4Cl + 2(C^{10}H^{11}O,CO^2):$$

but the formation of the latter compound was not actually observed]. (A. Wurtz, *N. J. Pharm.* 20, 14; *Ann. Pharm*, 79, 280) ¶.

*Combinations.*— Fusel-oil shaken up with *water*, takes up a small quantity of it, increasing thereby in density. (Pelletan, Apjohn.) The water at the same time dissolves a small portion of the fusel-oil, acquiring its odour and diminishing somewhat in density. (Pelletan.) According to Apjohn and Balard, fusel-oil does not dissolve in water.

It dissolves *phosphorus* at a boiling heat, forming a lemon-yellow solution (in small quantity, according to Trautwein), from which the phosphorus does not separate out on cooling. (Pelletan.)

It dissolves a small quantity of *sulphur* when heated (none, according to Trautwein, even at a boiling heat), the sulphur being precipitated on cooling. (Pelletan.)

It dissolves *iodine* abundantly. (Pelletan, Trautwein, *Repert.* 91, 28.)

It dissolves in strong *hydrochloric acid.* (Balard.)

It absorbs *ammoniacal gas* with green colour. (Pelletan.)

It dissolves a large quantity of *hydrate of potash,* acquiring first a yellow, then a greenish, then a deep red colour, and an offensive odour. Water forms with this solution an emulsion, from which the fusel-oil separates. (Pelletan.)—With *hydrate of soda* it forms a red solution, and if it contains a little water, a buttery mass. (Pelletan.)

It combines with *chloride of calcium.*

With *bichloride of tin,* it assumes a red colour, and yields crystals, which are decomposed by water, slowly even by the moisture of the air, yielding aqueous bichloride of tin and unaltered fusel-oil. (Gerhardt, *Ann. Chim. Phys.* 72, 167.)

From solution of gold, it extracts in a few days all the *chloride of gold.* (Pelletan.)

It mixes with *ether.* (Pelletan.)

It mixes in all proportions with *alcohol* (Apjohn), and is separated therefrom by water only, when the proportion of alcohol is small. (Pelletan.) This solution, and even brandy containing fusel-oil, assumes a carmine-colour when mixed with oil of vitriol. (Pelletan.)

Fusel-oil mixes in all proportions with strong *acetic acid,* and is not separated therefrom by potash-ley, because it is soluble in aqueous *acetate of potash.* (Pelletan.)

Fusel-oil mixes with *oils* both *fixed* and *volatile,* dissolves solid *fats,* common *camphor,* many *hard resins,* and, at high temperatures only, a small quantity of caoutchouc. (Pelletan.)

## Valeraldide.

$C^{10}H^{10}O^2 = C^{10}H^{10},O^2.$

Dumas & Stas. *Ann. Chim. Phys.* 73, 145; also *J. pr. Chem.* 21, 289.

Gaultier de Claubry. *Compt. rend.* 15, 171; also *Ann. Pharm.* 44, 127.

Trautwein. *Repert,* 91, 6.

Chancel. *Compt. rend.* 21, 934; also *J. pr. Chem.* 36, 447.

Keller. *Ann. Pharm.* 72, 31.

Parkinson. *Ann. Pharm,* 90, 114; abstr. *J. pr. Chem.* 62, 286; *Pharm. Centr.* 1854, 569; *Jahresbus* 1854, 442.

*Valerianic Aldehyde, Valeral, Mylaldid, Amylaldehyd, Baldrianaldehyd, Aldehyde valerique.*

*Formation.* 1. By the distillation of fusel-oil with oil of vitriol, (together with amylene and amylic ether.) (Gaultier.) — 2. By the action of strong nitric acid upon fusel-oil. (Dumas & Stas.) — 3. By the dry distillation of valerate of baryta. (Chancel.) — ¶ 4. By the dry distillation

of a mixture of valerate and formiate of lime in equal numbers of atoms:

$$C^{10}H^9CaO^4 + C^2HCaO^4 = 2(CaO,CO^2) + C^{10}H^{10}O^2.$$

Similarly, any aldide may be obtained by distilling the lime or baryta-salt of the corresponding fatty acid with an equivalent quantity of the formiate. (Limpricht, *Ann. Pharm.* 97, 368.) ¶ — 5. In the distillation of bran with sulphuric acid and peroxide of manganese, many other products being formed at the same time. (Keller.) When lupulin, the yellow powder, which falls out on rubbing the cones of the hop, is distilled with water, valerianic acid passes over together with a volatile oil. The latter is resinised by contact with the air; and the resinous mass distilled at a gentle heat with hydrate of lime yields valeraldide. (Personne, *N. J. Pharm.* 26, 241; *Compt. rend.* 38, 309.)

*Preparation.* 1. The distillate obtained from fusel-oil and oil of vitriol is repeatedly rectified, the less volatile liquids being each time set aside. (Gaultier.)—2. The mixture of fusel-oil and strong nitric acid is saturated with an alkali, after the violent evolution of heat has subsided, then distilled, and the oil which passes over collected. (Dumas & Stas.) — 3. Peroxide of manganese or aqueous bichromate of potash is added to a mixture of fusel-oil and strong sulphuric acid, and the oil which rises to the surface taken off. (Dumas & Stas.) — Or, 4 At. peroxide of manganese are added to a cooled mixture of 1 At. fusel-oil and 4 At. strong sulphuric acid contained in a tubulated retort; the distillation, which at first goes on of itself, assisted towards the end by a gentle heat; the slightly acid distillate redistilled after addition of carbonate of potash; and the oil separated from the water which has passed over with it. (Trautwein.) ¶. Or, 11 pts. of pure amylic alcohol are gradually mixed with $16\frac{1}{3}$ pts. oil of vitriol, previously diluted with an equal volume of water, and the mixture after cooling, gradually added to an aqueous solution of $12\frac{1}{3}$ pts. of bichromate of potash in a tubulated retort, whereby sufficient heat is evolved to distil over the greater part of the liquid, external heat being required only towards the end of the operation. The upper oily layer of the distillate is then separated from the lower liquid, washed with potash to free it from valerianic acid, and agitated with a perfectly saturated solution of bisulphite of soda, whereupon a crystalline compound of valeraldide with that salt separates out. The crystalline mass is then strongly pressed and dissolved in warm water at 70° to 80°; any oily liquid that may yet remain removed; the crystalline compound which separates on cooling, mixed in a retort with a concentrated solution of carbonate of potash or soda, and gently heated; and the valeraldide which rises to the surface as an oily layer, distilled off, separated from the water which passes over with it, and rectified. (Parkinson.) ¶. — 4. Valerate of baryta is distilled at a dull red heat, and the resulting oily mixture of about 9 pts. valeral and 1 pt. valerone repeatedly rectified, the valeral, which is the more volatile, being collected apart. (Chancel.)

*Properties.* Colourless oil. (Dumas & Stas; Gaultier; Parkinson.) Mobile; of sp. gr. 0·820 at 22° (Chancel); 0·818 (Trautwein); 0·8009 at 20°. (Personne.)— Boils at 96° (Gaultier), a little above 100°, and yields a vapour whose density is 2·93 (Chancel); at 96° to 97° (Parkinson); at about 90°. (Personne.) Smells like apples (Dumas & Stas); has a sharp penetrating odour (Gaultier); pleasant, but strong and peculiarly suffocating (Parkinson); produces oppression when inhaled (Gaultier),

and excites coughing (Trautwein); its vapour diffused in an apartment smells fruity at first, afterwards like valerianic acid. (Trautwein.) Its taste is strongly bitter (Gaultier); burning (Chancel); sharp and bitter. (Parkinson.) Neutral. (Dumas & Stas.) Refracts light strongly. (Parkinson.)

| | | | Dumas & Stas. | Chancel. | Keller. |
|---|---|---|---|---|---|
| 10 C | 60 | 69·77 | 70·07 | 69·56 | 69·51 |
| 10 H | 10 | 11·63 | 11·60 | 11·54 | 11·79 |
| 2 O | 16 | 18·60 | 18·33 | 18·90 | 18·70 |
| $C^{10}H^{10}O^2$ | 86 | 100·00 | 100·00 | 100·00 | 100·00 |

| | Vol. | Density. |
|---|---|---|
| C-vapour | 10 | 4·1600 |
| H-gas | 10 | 0·6930 |
| O-Gas | 1 | 1·1093 |
| Vapour of Valeraldide | 2 | 5·9623 |
| | 1 | 2·9811 |

*Decompositions.* 1. Valeraldide is very inflammable and burns with a bright flame faintly bordered with blue. (Chancel.) — 2. In contact with oxygen gas and platinum-black, and by other oxidising agents, it is converted into valerianic acid. (Chancel.) Also by exposure to the air (Gerhardt, *N. Ann. Chim. Phys.* 7, 279; Parkinson); and when kept for a month in vessels containing air, it acquires the power of reddening litmus. (Trautwein.) — 3. By nitric acid of ordinary strength, it is converted, with violent evolution of nitrous vapour, nitric oxide, and a gas which burns with a very bright flame, into a liquid which sinks in water and appears to be nitrovalerianic acid. (Chancel.) — 4. When valeraldide is heated with a dilute solution of bichromate of potash, valerianic acid passes over. — 5. When repeatedly distilled with dilute sulphuric acid and peroxide of manganese, only a small portion of it is converted into valerianic acid. (Trautwein.) — 6. Fused with hydrate of potash, it gives off hydrogen and forms valerate of potash. (Gerhardt.)

$$C^{10}H^{10}O^2 + KO + HO = C^{10}H^9KO^4 + 2H.$$

But it is not decomposed by boiling with potash-ley of sp. gr. 1·333. (Trautwein.)

*Combinations.* Insoluble in water. (Chancel, Parkinson).— Dissolves a tolerably large quantity of *phosphorus;* no sulphur, even at the boiling heat; and a very large quantity of *iodine.* (Trautwein.)

Mixes with *oil of vitriol.* (Gaulthier.)

*Valeraldide-ammonia.* A mixture of valeraldide and aqueous ammonia, which is turbid at first, soon becomes clear and deposits a large number of shining octohedrons. These crystals contain a large quantity of water of crystallization, which they gradually lose in vacuo, over a mixture of sal-ammoniac and lime. (Keller.) — ¶. Valeraldide absorbs ammoniacal gas rapidly and with great evolution of heat, producing a thick syrup; which, after standing for some weeks, is converted into a mass of delicate prismatic crystals. By exposure to the air or by heat, these crystals are quickly reconverted into the syrupy liquid. They are insoluble in water, but dissolve readily in alcohol and ether. (Parkinson.) — According to Limpricht (*Ann. Pharm.* 90, 111), the valeraldide obtained by oxidation of fusel-oil forms a definite compound with ammonia; but that which is produced by the dry distillation of valerate of baryta does not form any such compound. Similarly with butyraldide. Hence Limpricht concludes that the products obtained by the dry distillation of the

earthy propylates, butyrates, valerates, &c. are not identical, but merely isomeric with the true aldides produced by oxidation of the corresponding alcohols? he accordingly distinguishes them by the terms propylal, butyral, valeral, &c., restricting the term aldehyde [or aldide] to the bodies which form definite compounds of ammonia. He observes, however that the butyral with which he experimented was contaminated with butyrone. (compare x, 551).

| | | | Keller. | Parkinson. |
|---|---|---|---|---|
| 10 C | 60 | 58·25 | 57·84 | |
| N | 14 | 13·59 | 15·50 | 13·41 |
| 13 H | 13 | 12·62 | 12·84 | |
| 2 O | 16 | 15·54 | 13·82 | |
| $NH^3,C^{10}H^{10}O^2$ | 103 | 100·00 | 100·00 | |

Valeraldide-ammonia is converted by sulphuretted hydrogen into valeraldine $C^{30}NH^{31}S^4$, a compound homologous with thialdine. (Beissenhirtz, *Ann. Pharm.* 94, 109; Parkinson.)

$$3(NH^3,C^{10}H^{10}O^2) + 6HS = C^{30}NH^{31}S^4 + 6HO + 2NH^4S.$$

Hydrocyanic acid, in presence of dilute hydrochloric acid, and with the aid of heat, converts valeraldide-ammonia into leucin. (Limpricht, *Ann. Pharm.* 94, 243; Parkinson);

$$[NH^3,C^{10}H^{10}O^2 + C^2NH + HCl + 2HO = C^{12}NH^{13}O^4 + NH^4Cl.]$$

*Valeraldide with Bisulphite of Soda.* — *Preparation.* (p. 18.) — White crystalline mass consisting of nacreous laminæ. When left for some time in vacuo over oil of vitriol, it gives off its water of crystallization and crumbles to a white powder. When distilled with a concentrated solution of carbonate of potash or soda, it gives off valeraldide. Dissolves sparingly in cold water, more readily in water of 70° to 80°. On heating the aqueous solution to between 80° and 90°, decomposition takes place, valeraldide and sulphurous acid being given off, and sulphite of soda remaining in solution. The compound is nearly insoluble in absolute alcohol and in ether. (Parkinson.)

| | | | Parkinson. |
|---|---|---|---|
| $C^{10}H^{10}O^2$ | 86·0 | 43·17 | |
| NaO | 31·2 | 15·66 | 15·46 |
| 2 $SO^2$ | 64·0 | 32·13 | 31·95 |
| 2 HO | 18·0 | 9·04 | |
| $C^{10}H^{10}O^2,NaO,2SO^2 + 2Aq.$ | 199·2 | 100·00 | ¶. |

Valeraldide mixes in all proportions with *alcohol, ether,* and *volatile oils.* (Chancel.)

It dissolves certain *resins.* (Trautwein.)

¶ *Metavaleraldide?* — According to Parkinson, valeraldide heated above its boiling point, is converted into a liquid of the same composition, but boiling between 150° and 200°; the same modification appears also to be present in the liquid expressed from the sulphite of soda compound, and is likewise separated when this compound is heated with dry carbonate of soda. Limpricht however did not obtain such a modification by either of these three processes.¶

## Valerianic Acid.

$C^{10}H^{10}O^4 = C^{10}H^{10},O^4$.

CHEVREUL. *Ann. Chim. Phys.* 7, 264; 23, 22; also *Schw.* 39, 79. *Recherches sur les corps gras*, 99 and 200.
GROTE. *Br. Arch.* 33, 160; 38, 4.
TROMMSDORFF. *N. Tr.* 24, 1, 134; 26, 1, 1; abstr. *Ann. Pharm.* 6, 176.
WINCKLER. *Repert*, 44, 180; — 78, 70.
TRAUTWEIN. *Kastn. Arch.* 26, 282; *Repert.* 91, 28.
DUMAS & STAS. *Ann. Chim. Phys.* 73, 128; also *Ann. Pharm.* 35, 145; also *J. pr. Chem.* 21, 278.
LOUIS LUCIEN BONAPARTE. *J. Chim. méd.* 18, 6, 6; also *J. pr. Chem.* 30, 302.
WITTSTEIN. *Repert.* 87, 289;
ILJENKO & LASKOWSKY. *Ann. Pharm.* 55, 78.

***Valeric acid, Baldriansäure, Delphinsäure, Phocensäure, Acide valerianique, Ac. valerique, Ac. delphinique, Ac. phocenique.*** — First obtained from dolphin oil and exactly investigated by Chevreul in 1817. The acid discovered in valerian root by Pentz (*Br. Arch.* 28, 338) in 1819, and by Grote in 1830, and specially examined by Trommsdorff, as also that obtained by Dumas and Stas, from fusel-oil, were soon recognized as identical with delphinic acid.

*Sources.* 1. In *Valerian root.* To the amount of not quite 1 per cent. (Trautwein.) Both in the fresh and in dried root. (Grote.) It exists most abundantly in the small valerian root (Bonaparte), which is gathered in dry places in the spring. (Aschoff.) The herb of valerian contains very little acid. (Grote.) When the root is distilled with water, the acid passes over, partly in the state of aqueous solution, partly mixed with a neutral oil.

2. In the ripe berries (Chevreul), and in the bark (Krämer, *N. Br. Arch.* 40, 269; Moro, *Ann. Pharm.* 55, 330), of *Viburnum Opulus*, and in the alburnum of *Sambucus nigra.* (Krämer, *N. Br. Arch.* 43, 21.)

3. In the root of *Angelica Archangelica.* (Meyer & Zenner, *Ann. Pharm.* 55, 317) and of *Athamanta Oreoselinum.* (Winckler.) In *Asa fœtida.* (Hlasiwetz.)

4. In the oils obtained by distillation of the flowers of *Anthemis nobilis*, the more volatile portion which distils below 210° consisting chiefly of an oil composed of $C^{20}H^{16}$, and the portion which distils at and above 210°, yielding, when heated for a short time with alcoholic potash, the rest of the oil $C^{20}H^{16}$, while valerate and angelate of potash remain behind. (Gerhardt, *N. Ann. Chim. Phys.* 24, 96; also *Ann. Pharm.* 67, 238; also *J. pr. Chem.* 45, 221; *comp.* Schindler. *N. Br. Arch.* 41, 32.)— Peretti, (*J. Chim. méd.* 21, 433) and Dumenil (*Repert.* 86, 176) likewise obtained from the water distilled from the herb of *Matricaria Parthenium*, and of *Artemisia Absinthium*, a volatile acid which is perhaps valerianic acid.

5. The herb of *Digitalis purpurea* and other scrophulariaceous plants yielded to Pyr. Morin, (*N. J. Pharm.* 7, 299) a volatile acid, for which

in case of its not being valerianic acid, which it greatly resembles, he suggests the name: *Antirrhinic acid.*

6. As valerin, in the oil of *Delphinus globiceps*, and, although in much smaller quantity, in train-oil. (Chevreul.) Apparently also in animal secretions (Balard, *N. Ann. Chim. Phys.* 12, 317; see also Brendecke, *Arch. Pharm.* [2], 70, 34.

7. Valerianic acid appears sometimes to exist in crude oil of amber. (Marrson, *Arch. Pharm.* [2], 72, 1.)

*Formation.* 1. By the oxidation of fusel-oil, valeraldide, and various other compounds of the amylene series, by the action of the air, of nitric acid, chromic acid, hydrate of potash, &c. (Dumas & Stas, Balard.) — Hence also, when the residue of the distillation of wine-brandy, which contains fusel-oil, is left to putrefy in the air. (Balard, Laroque, *N. J. Pharm.* 10, 103. Railton (*Chem. Soc. Qu. J.* 6, 205,) finds that fusel-oil is converted into valerianic acid by passing a stream of oxygen gas through it.

2. By the putrefaction of most azotised organic bodies. —When pure casein is left to putrefy in summer in contact with water, valerate and butyrate of ammonia are formed, besides other products. (Iljenko, *Ann. Pharm.* 63, 264; see also Brendecke, x, 79.) — The parings of very old Roquefort cheese yield, when distilled with dilute sulphuric acid, an acid which smells like valerianic acid. (Balard.) — Strong-smelling Limburg cheese contains valerate of ammonia besides other ammoniacal salts. (Iljenko & Laskowsky; *comp.* x, 79.)— Rebling observed that butyric and valerianic acid were formed, besides succinic acid, by the fermentation of malate of lime, in contact with putrefying cheese, (*Arch. Pharm.* [2], 67, 300; *Pharm. Centr.* 1852, 63; in the latter place it is remarked that the valerianic acid may have been formed by the putrefaction of the cheese.) — Valerianic and butyric acid have been found in wheat spoiled by sea-water. (L. L. Bonaparte, x, 78.) — In the preparation of carthamin from safflower, there is sometimes formed in summer, a large quantity of valerianic acid, the carthamin at the same time diminishing considerably (Salvétat, *N. Ann. Chim. Phys.* 25, 337; also *N. J. Pharm.* 15, 269; also *J. pr. Chem.* 46, 475.) Valerianic acid is likewise found in putrefied ox-bile. (L. A Buchner, *J. pr. Chem.* 46, 151.) It is also obtained by distilling lupulin with water. (Personne, p. 18.)

3. By distilling gelatin (Schlieper, *Ann. Pharm.* 59, 1) or fibrin, albumin or casein (Guckelberger, *Ann. Pharm.* 64, 39), with chromate of potash and dilute sulphuric acid; and by the distillation of casein (Guckelberger) or gluten (Keller, *Ann. Pharm.* 72, 24) with sulphuric acid and oxide of manganese.

4. When hydrate of potash is fused with leucin or casein till hydrogen is given off, as well as ammonia, a residue is left containing valerate of potash. (Liebig, *Ann. Pharm.* 57, 127.)—A certain quantity of this acid appears also to be formed when commercial indigo or lycopodium seed is fused with hydrate of potash, probably in consequence of the protein-compounds contained in these bodies (*vid.* Gerhardt, *N. J. Pharm.* 1, 319; Winkler, *Repert* 78, 70).

5. In the oxidation of oleic acid by nitric acid, and of certain hydrocarbons by nitric acid or hydrate of potash. When oleic acid is distilled with fuming nitric acid, a large quantity of valerianic acid distils over, together with many other acids. (Redtenbacher.) — The more volatile portion of the mixture of empyreumatic oils obtained in the distillation

of rape-oil, yields, when distilled with strong nitric acid, a number of acids, among which is valerianic acid; and when passed in the state of vapour over heated soda-lime, it likewise forms a small quantity of valerate. (Schneider, *Ann. Pharm.* 70, 113.)

Unsuccessful attempts to prepare valerianic acid from acetic acid and valerian oil are described by Trautwein. (*Kastn. Arch.*, 27, 459.)

*Preparation.* 1. *From Valerian root.* — 1. The root is distilled with water; the acid oil separated from the water which distils over, and has likewise an acid reaction; the oil shaken up with water and carbonate of magnesia; the mixture distilled, whereupon a neutral oil passes over, and valerate of magnesia remains; and the valerianic acid separated from this salt by distillation with sulphuric acid. The acid watery distillate is likewise neutralised with carbonate of soda; the solution evaporated in a basin, whereby the neutral oil is partly volatilized, diffusing a strong odour of valerian, and is partly resinized to a brown film; the liquid filtered, and evaporated till it acquires a thickish consistence; this viscid liquid distilled with a quantity of oil of vitriol (diluted with one-half water) somewhat greater than is required to saturate the soda, the distillation being continued as long as the liquid which passes over continues to redden litmus; and the resulting layer of oil, which still contains a large quantity of water, decanted from the subjacent aqueous acid, and rectified by itself, the receiver being changed as soon as the clear oily anhydrous [monohydrated] acid passes over in place of the milky liquid. (Trommsdorff.) — In this process there is sometimes left in the retort a small quantity of oil or resin, which does not show itself in a second distillation of the anhydrous acid; neither does any milky liquid pass over at the beginning. — The acid cannot be dehydrated by distillation over chloride of calcium without becoming contaminated with hydrochloric acid. (Trommsdorff.)

2. Twenty parts of the comminuted root are distilled with 100 pts. of water, till 30 pts. of distillate are obtained; 30 pts. of water added to the residue, and then distilled off; the same process repeated once more; the three distillates saturated with carbonate of soda, after separation of the oil; the mixture boiled down to 7 parts in a copper vessel; the residue evaporated to dryness in a porcelain basin; the solution of 5 pts. of the residue in 5 pts. of water, mixed with 4 pts. oil of vitriol and 8 pts. water, and distilled nearly to dryness in a retort of eight times the capacity of the mixture; and the oily acid still containing water, removed from the watery distillate, and dehydrated by Trommsdorff's method. (Wittstein.) — After the three distillations with water, the root is exhausted of valerianic acid, but the residue is still strongly acid from the presence of a fixed organic acid (malic acid, according to Aschoff); there is therefore no necessity to add sulphuric acid for the purpose of separating the portion of valerianic acid supposed to be combined with bases. (Wittstein.) — 3. One part of the root cut in pieces is rapidly distilled with 4 pts. of water till 2 pts. have passed over; 2 pts. of hot water added to the residue; the distillation repeated; and the same treatment continued as long as the water continues to pass over acid. The whole of the watery and oily distillate is then gradually mixed at the boiling heat with a quantity of carbonate of soda sufficient to produce slight alkaline reaction; the liquid evaporated to about one-fourth, and filtered through coarse paper; the resinous powder which then remains, again boiled with aqueous carbonate of soda; the filtrate thence obtained

mixed with the preceding; and the mixture, after evaporation to one-half, distilled nearly to dryness with oil of vitriol and sulphate of soda, which serves to raise the boiling point. (Frederking, *N. Br. Arch.* 43, 2.) — 4. The well bruised root is distilled with eight times its weight of water; the oil which passes over freed by milk of lime from the acid which it contains; the watery distillate, which contains by far the greater part of the acid, then saturated with this milk of lime; the aqueous solution of valerate of lime mixed with a slight excess of lime and evaporated till a saline film forms on the surface, and decomposed in a stoppered bottle with excess of acetic acid; and the still coloured oily acid which rises to the surface, decanted off, and distilled at a gentle heat. (Bonaparte.) — Guillermond (*Rev. scient.* 19, 70,) extracts the acid from the oil with potash-ley. — 5. Sixteen parts of the root are boiled with water containing 1 pt. of carbonate of soda; the liquid strained, with pressure; the residue boiled twice more with water; the three united decoctions distilled with 0·5 pt. oil of vitriol, till $\frac{3}{5}$ of the liquid has passed over; and the distillate neutralised with carbonate of soda, evaporated down to a small quantity, and again distilled with sulphuric acid. This process yields 1·4 p.c. valerianic acid, that is to say, three times as much as is obtained by the troublesome distillation of the entire root. (T. & H. Smith, *Pharm. J. Trans.;* also *N. J. Pharm.* 11, 16.) — 6. Winckler's mode of preparation, in which the watery distillate of the cold aqueous infusion of the root is saturated with oxide of lead, and then the lead-salt converted into a soda-salt by means of sulphate of soda, &c., &c., does not appear to present any advantages.

The greater part of the valerianic acid contained in the root is united with a base which hinders the volatilisation. If therefore the root be distilled merely with water, it yields only 0·25 p.c. valerianic acid, and the residue distilled with water and sulphuric acid yields 0·75 p.c. more; 100 pts. of the root should therefore be distilled with water and 2 pts. of oil of vitriol, till 300 pts. of distillate are obtained; the acid extracted from the separated oil with aqueous carbonate of soda; the watery portion of the distillate saturated with this liquid; the mixture evaporated down to 10 pts.; and the concentrated liquid distilled with a slight excess of sulphuric acid: this process yields from 0·9 to 1·0 p.c. valerianic acid. (Rabourdin, *N. J. Pharm.* 6, 310; Peretti, *J. Chim. méd.* 21, 433.) — According to Aschoff, (*N. Br. Arch.* 48, 274,) on the other hand, the distillation of the root with water and sulphuric acid yields apparently a little more valerianic acid than distillation with pure water, but only when the valerianic acid is contaminated with acetic acid and a small quantity of formic acid. The root should therefore be distilled with water alone, after one day's maceration; if it be macerated for twenty days, fermentation takes place, and acetic acid is produced, which increases the yield of valerianic acid in appearance only. — Compare also Wittstein (p. 23.)

The neutral part of the oil obtained by the distillation consists chiefly of the oil called borneene ($C^{20}H^{16}$), and of another oil, valerol ($C^{12}H^{10}O^2$), which crystallises near 0°, and, when exposed to the air, is converted into valerianic acid, with formation of carbonic acid. (Gerhardt, *N. Ann. Chim. Phys.* 7·275.) — Accordingly, the distillate obtained from 100 pts. of the root, 10 pts. oil of vitriol, and 400 pts. of water, should be exposed to the air for four weeks, after which, when saturated with hydrated oxide of zinc, it yields 1·5 pts. of valerate of zinc, whereas, if the air has not acted upon it, only 0 5 pt. of zinc-salt is obtained. (Brun-Buisson, *N. J. Pharm.*, 9-97.)

— The product is rather diminished than increased by exposure to the air, in either case, the quantity of zinc-salt obtained amounts to rather more than 0·5 p.c. of the root, and the oil which is removed from the surface of the liquid does not yield any more valerianic acid when exposed to the air or treated with nitric acid. (Laudet, *N. J. Pharm.* 11, 444.) — The same oxidation is effected by chromic acid; 100 pts. of the root distilled with 10 pts. oil of vitriol, 6 pts. of bichromate of potash, and 500 pts. of water, — the 125 pts. which still pass over, and still contain a considerable quantity of unoxidised oil, being poured back again,—yield a distillate from which 1·8 pts. zinc salt are obtained. (Lefort, *N. J. Pharm.* 10, 194.) — This process yields but a very small quantity of valerate of zinc, contaminated with sulphate of zinc and the zinc-salt of a peculiar acid produced by oxidation of the valerianic acid. (Laudet.) — Water distilled from the root and neutralised with baryta becomes acid again on exposure to the air, and so several times. Valerian-oil purified from all free acid and mixed with water, becomes sour in a few weeks when exposed to the air, but not in close vessels, and its mixture with strong potash-ley is completely converted into valerate of potash by exposure to the air for a year. The root contains therefore, not valerianic acid, but valeral ($C^{10}H^{10}O^2$), which, when exposed to the air, especially in presence of water, and still more of alkalis, is converted by oxidation into valerianic acid. The root should therefore be mixed with potash-ley, and the mixture exposed to the air for four weeks, with frequent stirring, then distilled with sulphuric acid, &c., &c. (Thirault, *N. J. Pharm.* 12, 161; comp. Righini, *J. Chim. méd.* 21, 364; Lepage, *N. J. Pharm.* 9, 97.)

II. *From Angelica-root.* — The mother-liquor of angelic acid (x, 414) containing valerianic and acetic acid, is saturated with carbonate of baryta; the filtrate evaporated; the acetate of baryta extracted from the yellowish crystalline mass by alcohol; the portion which does not dissolve distilled with dilute sulphuric acid; and the valerianic acid which has passed over, freed from the still admixed angelic and acetic acid by saturation with ammonia and precipitation with nitrate of silver, whereupon the valerate of silver, being the least soluble salt present, separates in the largest proportion. (Meyer and Zenner.)

III. *From Dolphin-oil.* — 4 pts. of dolphin-oil are heated in the water-bath with 1 pt. hydrate of potash and 4 pts. of water, till a uniform translucent mass is produced, which forms a clear solution with water; this solution decomposed by excess of tartaric acid; the watery liquid separated from the stearic, margaric, and oleic acids thereby eliminated; and this liquid distilled, together with the wash-water of these three acids (the distillate being rectified, if it leaves any residue on evaporation), then saturated with crystals of baryta, and evaporated, whereupon it yields valerate of baryta. *a.* Either 100 pts. of the dry baryta-salt are stirred up with 205 pts. of phosphoric acid, of sp. gr. 1·12, in a narrow tube by means of a platinum wire; and the valerianic acid which rises in the form of an oil above the separated phosphate of baryta, together with an aqueous solution of acid phosphate of baryta, removed with the pipette and distilled at a gentle heat, whereupon nearly anhydrous valerianic acid passes over together with a small quantity of a heavier stratum, and a small quantity of brownish valerianic acid, altered by the action of the air, remains in the retort. — *b.* Or, a mixture of 33·4 pts. oil of vitriol and 33·4 pts. water is poured upon 100 pts. of dry baryta-salt contained in the tube; the yellowish oily acid which rises to the surface removed by a pipette;

33·4 pts. more of water added to the residue, whereby another portion of oily acid is separated, and may be removed by the pipette; the whole of the decanted acid distilled in the water-bath, a thick brownish yellow oil then remaining; and the acid which has passed over, separated from the watery layer. — For complete dehydration, 1 pt. of the acid is digested with 3 pts. chloride of calcium, and then distilled, whereby however the density is only reduced from 0·933 to 0·932 at 28°. (Chevreul.)

IV. *From Fusel-oil.* — 1. A mixture of 1 pt. fusel-oil and 10 pts. potash-lime is heated in a retort placed in a bath of fusible metal, first to 170°, then gradually to 200°, for 10 to 12 hours, till no more hydrogen is evolved; the mass left to cool in the closed retort; the retort then broken, and water quickly poured upon the mass, because it rapidly absorbs oxygen from the air and burns like tinder; the aqueous mixture poured into a new retort and distilled with dilute sulphuric acid; the valerianic acid collected in a receiver containing aqueous carbonate of soda; the valerate of soda thus obtained freed from undecomposed fusel-oil and valeraldide by boiling in a retort; and the valerianic acid, after addition of excess of phosphoric acid, distilled into a fresh receiver, and freed from the water which first passes over by a second rectification, the receiver being again changed. (Dumas and Stas.) [Why is not the fusel-oil, after being heated with potash-lime, immediately distilled with water and sulphuric acid in the first retort?]. — 2. A cold-saturated aqueous solution of bichromate of potash is mixed with oil of vitriol and then with fusel-oil, which is thereby converted, with evolution of heat and formation of chrome-alum, into valerianic acid and valerate of amyl which floats on the surface. The aqueous acid then yields by distillation the anhydrous [monohydrated] acid; and the valerate of amyl distilled with potash yields valerate of potash and fusel-oil, which may then be treated as before. (Balard, *N. Ann. Chim. Phys.* 12, 317.) — 3. Three atoms of coarsely-pounded bichromate of potash are mixed in a tubulated retort with 38 At. water; a mixture of 7 At. oil of vitriol and 1 At. fusel-oil poured in through an S-tube dipping into the water, rather quickly at first, but afterwards by drops as the mixture becomes hot; the mixture heated after the spontaneous evolution of heat has ceased, till a quantity of watery liquid and valeraldide, equal to $1\frac{1}{2}$ times the weight of the fusel-oil, has passed into the receiver; water poured upon the residue, and the distillation repeated; the whole neutralised by agitation with calcined magnesia; the valerate of amyl decanted off; the aqueous solution of valerianic acid and acetate of magnesia evaporated and mixed when cold with oil of vitriol diluted with a twofold quantity of water; and the valerianic acid which rises to the surface, pipetted off from the solution of sulphate of magnesia, in which the greater part of the acetic acid remains dissolved, and repeatedly rectified, with separation of the water and the heavier acetic acid [valerianic acid containing a larger proportion of water?], till its specific gravity is reduced to 0·930 at 17·5. There is also formed in the first retort a greyish green, porous, resinous mass of chromic valerate, which, after being collected on linen and washed with water, yields, by distillation with dilute sulphuric acid, an additional quantity of valerianic acid, to be purified by rectification. By this process, 2 pts. of fusel-oil yield in all, nearly 1 pt. of valerianic acid. (Trautwein, *Repert.* 91, 12.) — According to the equation :

$$3C^{10}H^{12}O^2 + 4(KO,2CrO^3) + 16SO^3 = 3C^{10}H^{10}O^4 + 4(KO,SO^3 + Cr^2O^3,3SO^3) + 6HO,$$

3 At. fusel-oil should require 4 At. bichromate of potash and 4 At. oil of vitriol, and should yield 3 At. valerianic acid; in Trautwein's process, the chromic acts in excess at the beginning, and a portion of the valerianic acid is thereby further decomposed. — ¶. H. Gruneberg (*J. pr. Chem.* 60, 169) pours $4\frac{1}{2}$ pounds of water on $2\frac{3}{4}$ pounds of chromate of potash in a retort, and allows a cooled mixture of 1 lb. fusel-oil and 4 lbs. oil of vitriol diluted with 2 lbs. water to run into the retort in a thin stream; he then distils once and calculates on a product of 9 oz. (18 loth.) of oily valerianic acid. ¶.

To separate a mixture of valerianic and butyric acids, it must be partially neutralized with potash and distilled. The butyric acid passes over, while valerate of potash remains behind; if too much potash be used, a certain quantity of butyrate of potash likewise remains; if the quantity of potash be too small, a portion of the valerianic acid likewise passes over; but the portion which remains mixed may be separated by a repetition of the process. If the valerianic (or butyric) acid is mixed with acetic acid, the latter remains as acid acetate of potash, when the liquid is partially saturated with potash and distilled, while the valerianic (or butyric) acid passes over. This is connected with the fact that valerianic acid does not dissolve in aqueous acid acetate of potash more abundantly than in water, but dissolves very abundantly in a solution of the neutral acetate, whereby acid acetate and neutral valerate of potash are produced. (Liebig, *Ann. Pharm.* 70, 352.)

*Properties.* Mobile, colourless oil. (Chevreul, Trommsdorff, & others.) Does not solidify at — 15° (Dumas & Stas; not even at — 21°. (Trommsdorff.) [The acid, which according to Grote, became turbid at — 8° and solidified in an unctuous mass at — 12·5° probably containing water.] Sp. gr. 0·930 at 12·5° (Trautwein), 0·932 at 28° (Chevreul), 0·937 at 16·5° (Dumas & Stas), 0·944 at 10° (Trommsdorff), 0·935 at 15°. (Delffs.) Index of refraction, for the red ray = 1·3952. (Delffs.) The acid leaves oily spots on paper, which gradually disappear on the application of heat. (Trommsdorff.) It boils at 132° under a pressure of 27·5 inches (Trommsdorff), at 175° (Dumas & Stas), at 176° (Bonaparte), at 174·5°, with the barometer at 237·8 mm. (Delffs.) [Trommsdorff's acid probably contained water, a conclusion warranted by its greater specific gravity.] Vapour-density = 3·67. (Dumas & Stas.) The true density is not attained till the temperature rises considerably above the boiling point, the density at lower temperatures appearing much too high. (Cahours, vii, 54, 55.) — The acid has an aromatic odour, like that of butyric acid, acetic acid and stale dolphin-oil, and imparts to fabrics moistened with it, the offensive odour of stale dolphin oil. (Chevreul.) Its odour differs somewhat from that of valerian-oil, and strongly excites coughing, especially when the acid is heated. (Grote.) Smells strongly and persistently like valerian (Dumas & Stas); smells more disagreeably than valerian, and at the same time like decayed cheese. (Wittstein, Nicklès.) — Has a very burning sour taste with an aromatically sweet after-taste, like that of apples or nitrous ether, and leaves a white spot on the tongue. (Chevreul.) Its taste is sour, sharp, and repulsive, and leaves a lasting impression on the tongue; but after dilution with water, it tastes less sharp and leaves a sweet after-taste (Trommsdorff); tastes very sour and sharp, and produces on the tongue and lips, a painful burning sensation, white spots, aud shrinking and solution of the skin. (Grote.) Tastes very acid and pungent, and leaves white spots on the tongue. (Dumas &

Stas.) Reddens litmus strongly (Chevreul); the reddening of the litmus-paper gradually disappears in a warm place. (Trommsdorff.)

| *The oily acid.* | | | | Ettling. | Dumas & Stas. | Salvétat. |
|---|---|---|---|---|---|---|
| 10 C | | 60 | 58·82 | 58·35 | 59·25 | 58·77 |
| 10 H | | 10 | 9·81 | 10·02 | 9·85 | 9·72 |
| 4 O | | 32 | 31·37 | 31·63 | 30·90 | 31·51 |
| $C^{10}H^{10}O^4$ | | 102 | 100·00 | 100·00 | 100·00 | 100·00 |

| | Vol. | Density. |
|---|---|---|
| C-vapour | 10 | 4·1600 |
| H-gas | 10 | 0·6930 |
| O-gas | 2 | 2·2186 |
| Acid-vapour | 2 | 7·0716 |
| | 1 | 3·5358 |

Ettling examined the acid prepared by Trommsdorf from valerian; Salvétat that obtained from safflower.

The radical-theory likewise distinguishes a hypothetical anhydrous acid = $C^{10}H^9O^3 = \overline{V}a$.

*Decompositions.* ¶. 1. The vapour of the acid *passed through a red-hot tube* yields volatile products varying in quantity with the heat applied, and a large quantity of gas containing carbonic acid, carbonic oxide, hydrocarbons of the formula $C^nH^n$, and perhaps also in some experiments, marsh-gas. By absorbing the hydrocarbons with bromine-vapour, an oily liquid is obtained which begins to boil at 130°, and distils over for the most part between 136° and 156°. The rectification of this latter distillate yielded a liquid boiling between 143° and 145°, and agreeing in composition very nearly with the formula $C^6H^6Br^2$. (compare ix, 395.) The bromine-compound which distils over at the lower temperature is $C^4H^4Br^2$; and the $C^6H^6Br^2$ appears to be mixed with a small quantity of $C^8H^8Br^2$. The hydrocarbons formed in the decomposition of valerianic acid by heat are therefore ethylene, propylene, and perhaps also butylene. (A. W. Hofmann, *Chem. Soc. Qu. J.* 3, 210) ¶.—2. By *distillation in vessels containing air*, part of the acid is converted into an aromatic substance resembling that which is obtained in the dry distillation of valerates; this substance remains dissolved in the undecomposed acid which passes over, and may be obtained separately by redistilling the distillate with oxide of lead. (Chevreul).—3. The acid kept in a bottle containing air, slowly decomposes and acquires the odour of leather saturated with train-oil. (Chevreul.) — 4. When set on fire, it *burns* like a volatile oil (Chevreul); with a bright flame and without smoke or residue (Trommsdorff); with a white sooty flame. (Dumas & Stas.) — 5. By *chlorine gas*, it is converted, with great rise of temperature and formation of hydrochloric acid, in the dark into terchloro-valerianic acid, and in sunshine into quadrichloro-valerianic acid. (Dumas & Stas.) — By *iodine* and *bromine* it is not decomposed, even in sunshine (Dumas & Stas); by *fuming nitric acid* also, with which it mixes in all proportions, it is not decomposed, even on boiling, distillation, and cohobation. (Trommsdorff, Trantwein, Dumas & Stas.) ¶. According to Dessaignes (*Compt. rend.* 33, 164; *Ann. Pharm.* 79, 374), when valerianic acid is boiled for 18 days with hydrated nitric acid, [sp. gr. 1·525 ?] in such a manner that the condensed vapours may flow back again, the nitric acid also being

renewed from time to time, a portion only of the valerianic acid is decomposed; and of the products of its decomposition, the most abundant is an acid which, from its analysis, appears to be *nitrovalerianic acid* $C^{10}H^9NO^8$ but in physical properties agrees rather with *nitro-angelic acid* $C^{10}H^7NO^8$. This acid is produced, whether the valerianic acid used is of natural origin or prepared from fusel-oil. When the natural acid is used, there are likewise formed a deliquescent acid, and a neutral, crystalline, azotised body having a faint odour of camphor; the artificial acid also yields a neutral, azotised oil having the odour of camphor ¶. — 6. When valerianic acid is boiled with aqueous *perchloric acid*, no detonation takes place, but the valerianic acid which floats on the surface, acquires a yellow and afterwards a brown colour. (Trautwein.) — 7. Its solution in *oil of vitriol* becomes slightly coloured at 100°, boils at a stronger heat, with evolution of valerianic acid and sulphurous acid, then slowly blackens, emits an ethereal odour, and leaves a tolerably large quantity of charcoal. (Chevreul.) The pale red mixture when boiled, gives off the greater part of its acid undecomposed, together with small quantities of water and sulphurous acid; but there remains a small quantity of carbonaceous matter. (Trautwein.) The dark yellow mixture of the acid with fuming oil of vitriol gives off sulphurous acid and chars when heated. (Trommsdorff.)—8. Valerianic acid heated with anhydrous *phosphoric acid* is resolved into valerone and combustible gases. (Dumas & Stas.) For the decompositions of valerianic acid combined with potash and baryta by electricity and by heat, see these salts.

*Combinations.* With *water.*— *a Bihydrated Valerianic acid. Terhydrate of Valerianic acid*, according to the radical-theory, which assumes the existence of 1HO in the dry acid. The dry acid shaken up with a quantity of water much less than sufficient to dissolve it, takes up about 25 per cent. of water without losing its oily consistency, and rises to the surface of the excess of water which holds a portion of the acid in solution. (Trommsdorff.) The same oil rises to the surface when a valerate dissolved in water is decomposed by a stronger acid, or when a large quantity of syrupy phosphoric acid is added to the aqueous solution of the acid. (Dumas & Stas.) It likewise passes over when a valerate is distilled with dilute sulphuric or phosphoric acid. This hydrate has a higher specific gravity than the dry acid, = 0·950 according to Trautwein, and a lower boiling point. (Dumas & Stas.)

| | | | Dumas & Stas. | Iljenko & Laskowsky. |
|---|---|---|---|---|
| 10 C | 60 | 50 | 50·5 | 49·61 |
| 12 H | 12 | 10 | 10·1 | 9·76 |
| 6 O | 48 | 40 | 39·4 | 40·63 |
| $C^{10}H^{10}O^4,2HO$ | 120 | 100 | 100·0 | 100·00 |

*b. Aqueous Valerianic acid.*—The acid dissolves in 16 pts. of cold water (Grote); in 20 pts. (Wittstein); in 30 pts. of water at 18·2° (Chevreul); in 30 pts. of water at 12°. (Trommsdorff.) The solution has a much milder taste than the dry acid, and saccharine at the same time. (Wittstein.)

Dry valerianic acid dissolves a rather large quantity of *phosphorus*, being gradually rendered milky thereby. (Trautwein.)

It does not dissolve *sulphur*, even on boiling.

It mixes with *oil of vitriol*, producing rise of temperature, and is partly separated therefrom by addition of water. (Chevreul.) The solution

is pale rose-coloured. (Trautwein.) That formed with fuming sulphuric acid is of a deep yellow colour; the acid likewise dissolves readily in heated sulphuric acid of sp. gr. 1·5. (Trommsdorff.)

It dissolves *iodine* quietly, abundantly, and without evolution of heat, forming a brown-red solution (Trautwein); the solution saturated as completely as possible, has a deep yellow-brown colour, and on addition of water, deposits all the iodine, while a dark yellow liquid remains. (Trommsdorff.)

It mixes in all proportions with *bromine.* (Trautwein, Dumas & Stas.)

It mixes in all proportions with fuming *nitric acid* (Trautwein); dissolves sparingly in cold nitric acid of 35° Bm. (Chevreul.)

The *Valerates* or *Valerianates* are, for the most part, $= C^{10}H^{9}MO^{4}$. They are somewhat unctuous to the touch. In the dry state, they are inodorous, even at 100°; but when moist, especially if heated or exposed to the action of carbonic acid, they emit the odour of valerianic acid. (Chevreul.) They have a sweet taste, especially the valerates of the alkalis and earths (Grote, Dumas, & Stas), and a pungent after-taste. (Trommsdorff.) Those valerates which are soluble in water have a slight acid reaction. (Winckler.) When subjected to dry distillation, the valerates first give off undecomposed acid (Trommsdorff), then combustible gas, valeral and valerone. (Chancel.) They are decomposed, with separation of the oily acid, by phosphoric, sulphuric, hydrochloric, nitric, arsenic, acetic, succinic, malic, tartaric and citric acid, but not by benzoic acid. (Grote, Trommsdorff.) Many dissolve in water, some also in alcohol. (Trommsdorff.)

*Valerate of Ammonia.*—Valerianic acid forms with ammoniacal gas, crystals, which, when they take up a large quantity of ammonia, slowly deliquesce to a transparent and colourless syrup. (Chevreul.) The aqueous acid supersaturated with aqueous ammonia gives off ammonia when evaporated, and leaves an acid syrup, which, when supersaturated with ammonia and exposed to the air, solidifies in white needles united in radiated masses. These crystals have the odour of valerian, and a sweet, afterwards sharp taste like that of valerian; they turn acid on exposure to the air, melt very easily, and volatilise in white fumes, leaving a trace of charcoal. (Trommsdorff.) The acid saturated with dry ammoniacal gas and freed from excess of ammonia by gentle evaporation, solidifies in delicate, feathery, slightly acid crystals, which melt in a retort at 31°C. without evolution of ammonia; and then emit white acid fumes, condensing in drops which crystallise when brought in contact with ammoniacal gas. (Aschoff, *N. Br. Arch.*, 48, 274.) The dry salt is resolved by anhydrous phosphoric acid into valeronitrile ($C^{10}NH^{9}$) and water. (Dumas, *Compt. rend.* 25, 442.) It dissolves very readily in water and likewise in alcohol. (Trommsdorff.)

*Valerate of Potash.* — Potassium, gradually added to the dry acid, forms, with great rise of temperature and brisk evolution of hydrogen, a pulp, which on cooling solidifies in a mass consisting chiefly of valerate of potash. (Trommsdorff, Trautwein). — An aqueous solution of carbonate of potash slightly supersaturated with the acid, is evaporated, whereupon not only the excess of acid escapes, but likewise that which is expelled by the carbonic acid of the air; the residue is dissolved in alcohol, the solution filtered from the carbonate of lime; and the filtrate evaporated. (Chevreul.)

Grote and Trommsdorff omit the extraction with alcohol. The solution evaporated to a syrup does not crystallise but solidifies to a stiff paste (Grote); and leaves on further evaporation, a white saline mass (Trommsdorff); a gum. (Dumas & Stas.) The salt has a pungent, slightly alkaline taste, with a sweetish after-taste, and blues reddened litmus. (Chevreul.)

| | *Anhydrous.* | | Chevreul. | Trommsdorff. |
|---|---|---|---|---|
| KO | 47·2 | 33·67 | 34·47 | 33·7 |
| $C^{10}H^9O^3$ | 93·0 | 66·33 | | |
| $C^{10}H^9KO^4$ | 140·2 | 100·00 | | |

The salt melts with loss of water at 140°; blackens as the heat increases, and gives off vapours which smell at first of valerianic, afterwards of empyreumatic acetic acid and burn with a dense yellow flame; and leaves white carbonate of potash. (Trommsdorff.) The salt dissolved in water is decomposed, by the current of Bunsen's battery, into hydrogen gas, butylene, carbonic acid gas, an oily mixture of valyl and a compound ether, and carbonate of potash. (Kolbe.) Into a glass cylinder 11 inches deep and 2½ in. wide, is introduced a piece of copper foil, bent in a cylindrical form, touching the sides of the vessel, and having a copper wire proceeding from it, — and a thinner cylinder of platinum foil not touching the copper and having a platinum wire proceeding from it; the glass cylinder is closed with an airtight-fitting cork, through which pass the copper wire, the platinum wire, and a tube for pouring in the saturated aqueous solution of the pure salt (especially free from chlorine-compounds), and afterwards for letting out and receiving the evolved gas; and the wires are connected with the poles of a four-celled Bunsen's battery, the positive electricity entering by the platinum cylinder. A large quantity of hydrogen gas thus collects on the copper, together with monocarbonate and bicarbonate of potash, and on the platinum cylinder carbonic acid and butylene gases (x, 66) together with valerianic acid, and a neutral oil which rises in drops, and appears to be a mixture of valyl [butyl] = $C^8H^9$ [or rather = $C^{16}H^{18}$] with a compound ether of valerianic acid, probably valerate of butyl. (Kolbe, *Ann. Pharm.* 70, 316.) Valerate of potash distilled with arsenious acid yields an oily liquid having a disagreeable alliaceous odour, and resembling cacodyl. (Gibbs, *Ann. Pharm.* 86, 222.) The salt deliquesces very quickly in damp air (slowly, according to Trommsdorff), dissolves very readily in strong alcohol, and at 20°, in less than 3·9 pts. of absolute alcohol. (Chevreul.)

*Valerate of Soda.* — Prepared by Chevreul and Trommsdorff in the same manner as potash-salt. The solution evaporated to a syrup crystallises to a cauliflower-like mass; but, on account of the great deliquescence of the salt, only by spontaneous evaporation in dry air at 32° (not at 26°). (Chevreul.) So likewise in the drying chamber; but by evaporation at a stronger heat, there is obtained a white mass, which is unctuous to the touch; tastes sweet and like valerian; becomes very soft at 130°; melts at 140° without loss of acid, to a transparent and colourless liquid, solidifies to a white mass on cooling; and is decomposed like the potash-salt at a stronger heat. (Trommsdorff.) By the galvanic current, it is decomposed in the same manner as the potash-salt, but the bicarbonate of soda being but sparingly soluble and therefore more abundantly deposited, stops the current sooner. (Kolbe.) — The salt deliquesces in the air, and dissolves

very readily and abundantly in water and in alcohol, even when absolute. (Chevreul, Trommsdorff.) According to Trautwein, the evaporated solution solidifies in a radiated mass.

*Valerate of Baryta.* — Baryta-water neutralised with valerianic acid yields by spontaneous evaporation, transparent, shining, easily friable prisms (soft to the touch, according to Chancel) which grate between the teeth, have a warm, pungently alkaline taste, with a sweetish after-taste like that of valerian; slightly blue reddened litmus (from containing baryta set free by the evaporation: *Chancel*); and effloresce in the air between 20° and 25°, with loss of 2·41 p. c. water. (Chevreul.) The crystals contain 9·5 p. c. (2 At.) water of crystallisation, of which they give off from 2 to 2·5 p. c. on exposure to the air, and the rest at a higher temperature. (Chancel.) In the cold the prisms are permanent. (Trommsdorff.)

| *Dried at* 130°. | | | Ettling. | Chevreul. |
|---|---|---|---|---|
| BaO | 76·6 | 45·16 | 45·23 | 45·29 |
| 10 C | 60·0 | 35·38 | 35·59 | |
| 9 H | 9·0 | 5·31 | 5·28 | |
| 3 O | 24·0 | 14·15 | 13·90 | |
| $C^{10}H^9BaO^4$ | 169·6 | 100·00 | 100·00 | |

The dry salt begins to decompose above 250°, and is completely decomposed at a dull red heat, with continued evolution of a gas, probably butylene, which burns with a very bright flame, and a small quantity of pale yellow, strongly smelling distillate, which contains 70·7 p. c. C, 11·7 H, and 17·6 O, and may be regarded as a mixture of 9 pts. valeral (p. 17) and 1 pt. valerone ($C^{18}H^{18}O^2$), while carbonate of baryta remains, mixed with a small quantity of charcoal. (Chancel.)

$$2C^{10}H^9BaO^4 = C^{18}H^{18}O^2 + 2(BaO,CO^2);$$

but by the high temperature required for the decomposition of the baryta-salt, the greater part of the valerone ($C^{18}H^{18}O^2$) is resolved into valeral $C^{10}H^{10}O^2$, and butylene ($C^8H^8$). (Chancel). Chevreul obtained, together with a gas which he regarded as ethylene, a very small quantity of carbonic acid gas, an orange-yellow, strongly smelling liquid not acid or soluble in potash, and carbonate of baryta mixed with charcoal, amounting to 3·3 p. c. (of the valerate of baryta). — The salt heated in the air emits an odour like that of the *Labiatæ*. The dilute aqueous solution, when exposed to the air, deposits carbonate of baryta and flakes, and acquires the odour of Roquefort cheese. The salt dissolves in 2 pts. of water at 15°, and in 1 pt. water at 20°. (Chevreul.) It moves about on water like butyrate of baryta. (Larocque & Huraut.) It dissolves with difficulty in absolute alcohol. (Schlieper, *Ann. Pharm.*, 59, 21.)

*Valerate of Strontia.* — Strontia-water neutralised with the acid deposits a varnish-like residue when evaporated in the open air, but within a bell-jar containing air over lime, it yields long efflorescent prisms, which smell of valerianic acid; taste like the baryta-salt; dissolve very readily in water; and, in the dehydrated state, contain 36·54 per cent. of strontia. (Chevreul.) The saturated solution of carbonate of strontia in a warm mixture of 1 pt. acid and 12 pts. water, yields by gentle evaporation, elongated four-sided tables, which effloresce in warm air, and are soluble in alcohol. (Trommsdorff.)

*Valerate of Lime.* — The aqueous acid saturated at a moderate heat with carbonate of lime yields prisms and needles by slow evaporation. (Chevreul.) The crystals are united in stars; taste sweetish; effloresce only in warm air; soften at 149°; melt at 150°, with blackening and evolution of vapours, which burn with a bright flame, and leave carbonate of lime mixed with charcoal. They dissolve readily in water, and in boiling hydrated alcohol, sparingly in absolute alcohol. (Trommsdorff.) The crystals give off 6·6 p. c. water below 140°. (Winckler.)

| | *Dried at* 130°. | | Trommsdorff. | Chevreul. |
|---|---|---|---|---|
| CaO | 28 | 23·14 | 23·38 | 24·48 |
| $C^{10}H^9O^3$ | 93 | 76·86 | | |
| $C^{10}H^9CaO^4$ | 121 | 100·00 | | |

*Valerate of Magnesia.* — The aqueous acid saturated with carbonate of magnesia forms a neutral, very sweet solution, which by quick evaporation yields saline crusts; but by slow evaporation transparent prisms united in tufts. These crystals effloresce only in warm dry air, soften at 140°, then turn black and give off acid, and, after long ignition, leave pure magnesia. They dissolve pretty readily in water, sparingly in alcohol. (Trommsdorff.)

*Valerate of Glucina.* — The solution of carbonate of glucina in the aqueous acid tastes very sweet, with a somewhat astringent after-taste, and leaves on evaporation, first a tough film, then a gummy mass permanent in the air. (Trommsdorff.)

*Valerate of Alumina.* — Hydrate of alumina quickly absorbs the dry acid, forming a mass which gives up nothing to boiling water; the same mass is formed on bringing hydrate of alumina into the heated aqueous acid, or by precipitating sulphate or hydrochlorate of alumina with valerate of potash. This mass treated with hot water divides into flakes which quickly settle to the bottom, and on cooling solidify in a tallowy, very friable mass, having a slightly sweet taste. This mass dried at 130°, contains 15·26 p. c. alumina. Boiling water and aqueous valerianic acid dissolve only a trace of it; alcohol none. (Trommsdorff.)

*Valerate of Zirconia.* — The earth dissolves only in the boiling aqueous acid, and but very sparingly; the solution has a sweetish taste, reddens litmus strongly, and on evaporation gives off acid and leaves a dry, white amorphous mass, no longer perfectly soluble in water. (Trommsdorff.)

*Uranous Valerate.* — The solution of uranic valerate in excess of aqueous valerianic acid gives off a gas when exposed to the sun, and deposits uranous valerate in the form of a violet substance which, when dried in the air, is reconverted into a yellowish powder. (Bonaparte.)

*Uranic Valerate.* — 1 At. valerate of silver dissolved in water is precipitated by 1 At. chloride of uranous oxide, and the filtrate left to evaporate in a place not exposed to sunshine. There then remains a yellow shining varnish, which gives off its acid at a gentle heat, and dissolves very readily in water, alcohol and ether. (Bonaparte.)

*Manganous Valerate.* — The solution obtained by heating manganous carbonate with the aqueous acid yields by spontaneous evaporation, highly

lustrous rhombic tables, greasy to the touch and easily soluble in water. (Trommsdorff.)

*Valerate of Bismuth.* — The solution of nitrate of bismuth is precipitated by valerate of soda. (Righini, *J. Chim. méd.* 22, 405.)

*Valerate of Zinc.* — Zinc dissolves slowly in the aqueous acid. (Grote.) Sulphate of zinc mixed with valerate of soda yields the salt in laminæ. (Trommsdorff.) — The dilute acid is saturated by continued boiling (best in a retort to avoid loss) with carbonate of zinc, filtered at the boiling heat, and the filtrate evaporated to the crystallising point. Either the crystals which form each time the liquid cools are collected, or those which form from time to time during gentle evaporation. In this case also Frederking recommends the use of a retort, because part of the acid volatilises. — White nacreous scales, like those of boracic acid, having rather an astringent than a sweet taste, permanent in the air (Trommsdorff); they redden litmus. (Wittstein.) They contain 29·5 p. c. zinc-oxide. (Wittstein.) They melt at 140° to a syrup, without loss of acid, and when ignited give off dense white vapours, which burn with a blue zinc-flame (Trommsdorff), while oxide of zinc remains behind. (Wittstein.) They dissolve in 5 pts. of cold, in 40 pts. of boiling water, in 14·4 pts. of cold, and in 16·7 pts. of boiling alcohol (Duclou); they dissolve in 160 pts. of cold water and in 60 pts. of cold 80 p. c. alcohol; these cold solutions become turbid when heated, and clear again on cooling; hence the solubility in water and alcohol diminishes as the temperature rises; on the other hand, the crystals dissolve in 500 pts. of cold and in 20 pts. of boiling ether. (Wittstein.) — Compare further: Grote, Bonaparte, Frederking (*N. Br. Arch.* 43, 2; Guillermond & Duclou (*Rev. scientif.* 19, 70 & 71); Vuaflart (*N. J. Pharm.* 6, 219). — The adulteration of this salt with butyrate of zinc, which closely resembles it, is noticed by Larocque & Huraut, *N. J. Pharm.* 9, 430.)

*Valerate of Cadmium.* — The aqueous acid slowly dissolves carbonate of cadmium, and yields, by evaporation, laminæ resembling those of boracic acid, but having a still higher fatty lustre, and soluble in water and alcohol. (Bonaparte.)

*Valerate of Lead.* — *a. Tribasic.* — The dry acid combines rapidly and with great evolution of heat, with excess of finely-pounded lead-oxide, and on subsequently heating the product, it is found that 100 pts. of the acid have yielded 9 pts. of water. By exhausting the resulting mass with cold water, filtering from the lead-oxide which remains free, and evaporating the filtrate in vacuo over oil of vitriol, delicate, shining needles are obtained, united in hemispherical masses, infusible, and smelling slightly of valerianic acid. They absorb carbonic acid from the air, and dissolve sparingly in water. (Chevreul.)

*b. Monobasic.* — When the solution of lead-oxide in excess of aqueous valerianic acid is evaporated, with frequent addition of acid, so as to keep the acid in excess, the salt remains as a fusible amorphous residue; but by evaporation in vacuo over oil of vitriol, it is obtained in shining flexible laminæ. (Chevreul.) By quickly evaporating the solution to a syrup and cooling, a mass is obtained having the consistence of turpentine and capable of being drawn out into threads; by slow evaporation the salt is obtained in laminated crystals. (Grote.) The carbonate of lead dissolves slowly, and there is obtained a very sweet and afterwards astringent-tasting liquid, yielding, by quick evaporation, a viscid mass, and by

slower evaporation, white laminæ, both of which dissolve very readily in water. (Trommsdorff.)

| *Tribasic, anhydrous.* | | | Chevreul. |
|---|---|---|---|
| 3 PbO | 336 | 78·32 | 78 |
| $C^{10}H^9O^3$ | 93 | 21·68 | |
| $2 PbO,C^{10}H^9PbO^4$ | 429 | 100·00 | |

| *Monobasic, laminæ.* | | | Chevreul. |
|---|---|---|---|
| PbO | 112 | 54·64 | 55·5 |
| $C^{10}H^9O^3$ | 93 | 45·36 | |
| $C^{10}H^9PbO^4$ | 205 | 100·00 | |

*Ferrous Valerate.* — Iron filings immersed in the aqueous acid slowly eliminate hydrogen, and form a black-brown coagulum having a sweetish astringent taste. (Trautwein.)

*Ferric Valerate,* — *a. Mono-acid?* — Obtained by heating *b* to 100°, as long as it continues to lose weight. Brown powder. (Wittstein.)

*b. Bi-acid?* — An aqueous solution of sesquichloride of iron is precipitated by valerate of soda, free valerianic acid then remaining in the liquid; and the precipitate is washed with a small quantity of water and dried below 20°. Dark brick-red amorphous powder having somewhat of the smell and taste of valerian. By exposure to a slowly increasing heat, it gives off all its acid without melting; but when quickly heated, it melts, and gives off dense inflammable vapours, having scarcely any odour of valerianic acid but smelling rather like butyric acid. Gives off all its acid to boiling water, leaving pure ferric hydrate. Dissolves readily in hydrochloric acid. (Wittstein.)

| *Salt a dried at* 100°. | | | Wittstein. |
|---|---|---|---|
| $Fe^2O^3$ | 80 | 43·95 | 41·71 |
| $C^{10}H^9O^3$ | 93 | 51·10 | 53·12 |
| HO | 9 | 4·95 | 5·17 |
| $Fe^2O^3,C^{10}H^{10}O^4$ | 182 | 100·00 | 100·00 |

| *Salt b dried at* 20°. | | | Wittstein. |
|---|---|---|---|
| $Fe^2O^3$ | 80 | 28·17 | 26·85 |
| $2 C^{10}H^9O^3$ | 186 | 65·50 | 69·22 |
| 2 HO | 18 | 6·33 | 3·93 |
| $Fe^2O^3,2C^{10}H^{10}O^4$ | 284 | 100·00 | 100·00 |

The calculation does not quite agree with the analysis, and accordingly Wittstein prefers more complicated formulæ; but his method of estimating the anhydrous acid and the water cannot lead to accurate results.

*c. With excess of acid?*—By immersing iron wire for some time in the acid, and boiling the resulting dark red mass with water, a solution is obtained, on which however the greater portion of the product floats in the form of a dark red-brown oil. [salt *b*?] The solution gives a brown precipitate with potash. (Trommsdorff.)

*Valerate of Cobalt.*—The rose-coloured solution of carbonate of cobalt in warm dilute valerianic acid becomes covered with a red film when

evaporated, and dries up to a violet-red translucent mass. When the solution of this mass in water is evaporated to a syrup and set aside in the cold, violet-red, transparent prisms are produced, having a sweet, slightly astringent taste, permanent in the air, and easily soluble in water and alcohol. (Trommsdorff.)

*Valerate of Nickel.*—Carbonate of nickel dissolves with difficulty in the heated aqueous acid, whereas with the dry acid, it quickly forms a green oil. This oil dissolves very sparingly in water, forming a very pale green solution; but with alcohol it forms a pale green solution which, on evaporation, deposits a pale green powder, sparingly soluble in water. (Trommsdorff.)

*Cupric Valerate.*— The dry acid exposed to the air in contact with cupric oxide assumes a dark green colour in the course of some weeks; the hot aqueous acid forms with cupric carbonate a bluish green solution, which, on evaporation, yields green prisms permanent in the air, easily soluble in water and also in alcohol. (Trommsdorff.) [For the crystalline form see Schabus, *Jahresber*, vii, 442.] On adding the concentrated acid to aqueous cupric acetate, nothing appears at first; but on agitation, greenish oil-drops are produced, consisting of cupric valerate, which after 5 to 20 minutes, takes up water and changes to a green-blue crystalline powder. Valerianic acid mixed with butyric acid produces, when stirred up with a slight excess of cupric acetate, at first the green oil-drops, on which, as well as on the glass rod, there are deposited, after a while and without further turbidity, the pale blue scales of cupric butyrate. (Larocque & Huraut, *N. J. Pharm.* 9, 430.)

*Mercurous Valerate.*— The boiling thickened acid dissolves a small quantity of mercurous oxide, and yields small needles on cooling. (Grote.)

*Mercuric Valerate.*— Mercuric oxide dissolves in the heated oily acid, forming an oil which on cooling solidifies in a mass having the consistence of plaster; this mass is insoluble in cold, but soluble in hot water; the colourless solution deposits slender white needles on cooling, and the mother-liquor leaves on evaporation, a red mass insoluble in water and dissolving with red colour in the dry acid. The white slender needles which are likewise deposited on mixing valerate of potash with mercuric nitrate or chloride, are converted by moderate heating into a red basic salt, with loss of acid. (Trommsdorff.)

*Valerate of Silver.*— A solution of nitrate of silver is precipitated by a slight excess of an alkaline valerate. The precipitate, which is curdy at first, becomes crystalline after immersion for some time in the liquid (Ettling), and then resembles fulminating silver (Dumas & Stas); appears to consist of laminæ soft to the touch and having a silky lustre. (Winkler.) On evaporating the aqueous solution, the salt is obtained in white laminæ having a metallic lustre. (Ettling.) The salt blackens quickly in the light (but less quickly than acetate of silver according to Winckler) and must therefore be dried in the dark. (Dumas & Stas.) When heated, it emits vapours having the odour of valerian, then melts into a black mass, which suddenly emits extremely offensive vapours, and leaves pure white silver. (Winckler.)

| *At* 130°. | | | Ettling. | Moro. | Dumas & Stas. | Winckler. |
|---|---|---|---|---|---|---|
| 10 C | 60 | 28·71 | .... | 28·65 | 28·3 | |
| 9 H | 9 | 4·31 | .... | 4·33 | 4·3 | |
| Ag | 108 | 51·67 | 51·93 | 51·64 | 51·6 | 52·94 |
| 4 O | 32 | 15·31 | .... | 15·38 | 15·8 | |
| $C^{10}H^9AgO^4$ | 209 | 100·00 | .... | 100·00 | 100·00 | |

Ettling & Winckler examined the salt from valerian; Moro that from the bark of *Viburnum Opulus;* and Dumas & Stas, that obtained from fusel-oil.

Concentrated valerianic acid mixes in all proportions with *alcohol* and *ether*. (Chevreul, Grote, Dumas & Stas.) The solution in an equal quantity of absolute alcohol is rendered by a small quantity of water, and clear again by a larger quantity. (Trommsdorff.)

It dissolves abundantly in strong *acetic acid* of sp. gr. 1·07. (Trommsdorff.)

According to Trautwein, it mixes with *oil of turpentine* in all proportions; according to Grote, on the other hand, only partially (perhaps from containing water ?), and according to Trommsdorff, not at all; neither with olive-oil.

It dissolves *common camphor*. (Trommsdorff, Trautwein.)

It dissolves a few *resins*. (Trautwein.)

## ¶. Anhydrous Valerianic Acid.

$$C^{10}H^9O^3 \text{ or } C^{20}H^{18}O^6 = \left.\begin{matrix}C^{10}H^9O^2\\C^{10}H^9O^2\end{matrix}\right\}O^2$$

CHIOZZA. *Compt. rend.* 35, 568; *Ann. Pharm.* 84, 106; *J. pr. Chem.* 58, 23; *Chem. Gaz.* 1853, 52; *Jahresber.* 1852, 453.

*Valeric Valerate, Valeric Anhydride.*

Prepared by the action of 1 pt. oxychloride of phosphorus on 6 pts. valerate of potash (obtained in a state of purity by evaporating the alcoholic solution and melting the residue); the product, a thick oil, yields, when treated with a very dilute solution of carbonate of soda, and then with ether, an ethereal solution which leaves the anhydrous acid when evaporated.

Colourless, tolerably mobile oil, lighter than water. Boils without decomposition at about 215°. When recently prepared, it has a faint and rather unpleasant odour; when rubbed between the hands, it imparts to them a persistent odour of ordinary valerianic acid. Its vapour attacks the eyes and excites coughing. By boiling water it is converted slowly, and by alkalies quickly, into ordinary valerianic acid. With aniline it forms valeranilide $C^{22}NH^{15}O^2$. (Chiozza.) ¶.

## Sulphide of Amyl.

$C^{10}H^{11}S = C^{10}H^{10},HS.$

BALARD. *N. Ann. Chim. Phys.* 12, 294; also *J. pr. Chem.* 34, 132.

*Schwefelämyl, Schwefelmylafer, Ether sulfhydramylique.*

Chloride of amyl is distilled with an alcoholic solution of monosulphide of potassium — or better, the mixture, enclosed in a sealed glass tube is heated for some time [to 100° ?]; the liquid then decanted from the chloride of potassium, and the sulphide of amyl separated from it by addition of water.

Colourless liquid, boiling at 216°, having a vapour-density of 6·3 and a strong odour and taste of onions. (Balard.)

| | | | | | | Balard. |
|---|---|---|---|---|---|---|
| 10 C | 60 | .... | 68·97 | ........ | 68·25 |
| 11 H | 11 | .... | 12·64 | ........ | 12·65 |
| S | 16 | .... | 18·39 | ........ | 19·10 |
| $C^{10}H^{11}S$ | 87 | .... | 100·00 | ........ | 100·00 |

| | Vol. | | Density. |
|---|---|---|---|
| C-vapour | 10 | .... | 4·1600 |
| H-gas | 11 | .... | 0·7623 |
| S-vapour | $\frac{1}{6}$ | .... | 1·1093 |
| Vapour of $C^{10}H^{11}S$ | 1 | .... | 6·0316 |

[According to this, the vapour of sulphide of amyl is monatomic, like that of sulphide of ethyl (viii, 338). The atomic weight of these bodies, as well as that of the corresponding ethers, ought perhaps therefore to be doubled.]

## Amylic Mercaptan.

$C^{10}H^{12}S^2 = C^{10}H^{10},H^2S^2.$

KRUTZSCH. *J. pr. Chem.* 31, 1.
BALARD. *N. Ann. Chim. Phys.* 12, 294; also *J. pr. Chem.* 34, 133.
ERDMANN & GERATHEWOHL. *J. pr. Chem.* 34, 447.

*Amyl-mercapatan, Mylemercapatan, Amylsulfür-Schwefelwasserstoff, Mercaptan amylique.*

*Preparation.* 1. Purified fusel-oil is mixed, gradually and with agitation, with an equal weight of oil of vitriol; the mixture neutralised with aqueous carbonate of potash; the sulphamylate of potash which remains in solution filtered from the sulphate of potash; and the filtrate mixed with caustic potash, saturated with sulphuretted hydrogen, and distilled in the chloride of calcium bath in a capacious retort with a cooled receiver. The oily drops which float on the surface of the watery distillate are then removed with a pipette, set aside over chloride of calcium, and rectified after decantation. (Krutzsch.)

$$C^{10}H^{11}KO^2,2SO^3 + KS,HS = C^{10}H^{12}S^2 + 2\,(KO,SO^3).$$

When *crude* fusel-oil is used, a brown oil rises to the surface on the addition of the potash; and even if this be taken away, and then distilled after saturation with sulphuretted hydrogen, the resulting mer-

captan is still impure. (Erdmann & Gerathewohl.) — 2. Sulphamylate of lime is distilled with hydrosulphate of potassium. — 3. Chloride of amyl is distilled with an alcoholic solution of hydrosulphate of potassium — or better, the two substances are heated together in a sealed tube, and the amylic mercaptan separated as an oil rising to the surface by addition of water. (Balard.)

$$C^{10}H^{11}Cl + KS,HS = C^{10}H^{12}S^2 + KCl.$$

*Properties.* Colourless oil, of great refracting power, and sp. gr. 0·835 at 21°. (Krutzsch.) Boils at 117° (Krutzsch), at 117 to 118° (Erdmann & Gerathewohl), at 125°. (Balard.) Vapour-density = 3·631 (Krutzch), 3·9. (Balard.) Has a pungent alliaceous odour (Krutzsch), much more disagreeable than sulphide of ethyl, like that of sulphuretted hydrogen. (Balard.)

| | | | Krutzsch. | Balard. |
|---|---|---|---|---|
| 10 C | 60 | 57·69 | 57·29 | 58·25 |
| 12 H | 12 | 11·54 | 11·36 | 11·60 |
| 2 S | 32 | 30·77 | 30·55 | |
| $C^{10}H^{12}S^2$ | 104 | 100·00 | 99·20 | |

| | | |
|---|---|---|
| C-vapour | 10 | 4·1600 |
| H-gas | 12 | 0·8316 |
| S-vapour | $\frac{1}{3}$ | 2·2186 |
| Merc-vapour | 2 | 7·2102 |
| | 1 | 3·6051 |

*Decompositions.* 1. When kept in loosely closed bottles, it gives off sulphuretted hydrogen, and is converted into sulphide of amyl. (Balard.) — 2. On cold *nitric acid* of sp. gr. 2·25, amylic mercaptan floats at first almost unaltered; but on long standing or gentle heating, it turns red, then quickly becomes very hot and gives off nitrous fumes, and ultimately forms two layers, the lower of which contains nitric acid, amylosulphurous and a small quantity of sulphuric acid, while the upper is a variable oily mixture, sometimes lighter, sometimes heavier than water. A sample of this oil lighter than water contains 56·02 p.c. C, 10·38 H, 9·24 S and 24·36 O. (Erdmann and Gerathewohl.)

Amylic mercaptan combines with *lead-oxide*, forming a yellow flocculent mass, and when added to the acetate, throws down a coagulum of the consistence of turpentine. (Krutzsch.)

It does not act on *cupric oxide*, but throws down from the sulphate a greenish glutinous mass. (Krutzsch.)

With *mercuric oxide* it combines, with violent evolution of heat, forming a colourless liquid, which, on cooling, solidifies in a translucent lamino-radiated mass, which melts again at 100°, is not decomposed by boiling potash-ley, is not soluble in water, and but sparingly soluble in boiling alcohol and ether, whence it separates for the most part in scales on cooling. (Krutzsch.) Insoluble in water and alcohol, but soluble in ether. (Balard.) Its powder mixed with pounded glass and gently heated in a retort, yields, when sulphuretted hydrogen is passed through it, amylic mercaptam, which may be purified from adhering sulphuretted hydrogen by repeated rectification. But by decomposing with aqueous hydrochloric acid, only a small quantity of amylic mercaptan is recovered. (Erdmann & Gerathewohl.)

The compound with *silver-oxide* resembles mercaptide of silver, and is insoluble in water and alcohol, but soluble in ether. (Balard.)

## Bisulphide of Amyl? $C^{10}H^{11}S^2$?

O. Henry (1849). *N. Ann. Chim. Phys.* 25, 246; also *Compt. rend.* 28, 48; also *N. J. Pharm.* 14, 247; also *J. pr. Chem.* 46, 160.

*Doppeltschwefelamyl, Bisulfure d'Amyle.*

Crystalline amylosulphate of potash and a highly concentrated solution of bisulphide of potassium in about equal volumes, are distilled together in a retort of four times the capacity of the mixture, on account of the strong intumescence; and the yellowish oil which floats on the watery distillate is rectified two or three times over chloride of calcium.

The product is a pale yellow distillate, which boils at 210° to 240°, has a strong penetrating odour, — and another distillate of a fine yellow colour, which boils between 240° and 260°, has a specific gravity of 0·918 at 19°, and the same odour.

| | | | Henry. |
|---|---|---|---|
| 10 C | 60 | 58·25 | 58·90 |
| 11 H | 11 | 10·68 | 10·42 |
| 2 S | 32 | 31·07 | |
| $C^{10}H^{11}S^2$ | 103 | 100·00 | |

[Perhaps only a mixture of $C^{10}H^{12}S^2$ and $C^{10}H^{10}S^2$, a view which is confirmed by the rise of the boiling-point.]

Henry does not state the boiling-point of the sample which he analysed.

The oil, when decomposed by nitric acid, yields Erdmann and Gerathewohl's sulphamylosulphuric acid, (p. 52). (Henry.)

## Iodide of Amyl.

$C^{10}H^{11}I = C^{10}H^{10},HI.$

Cahours (1839). *Ann. Chim. Phys.* 70, 81; also *Ann. Pharm.* 30, 297.
Frankland. *Ann. Pharm.* 74, 42.

*Iodamyl, Iodmylafer, iodwasserstoffsaures Amylen, Hydriodate d'Amylene.*

*Preparation.* 1. Fifteen pts. of fusel-oil are distilled at a gentle heat with 1 pt. of phosphorus and 8 pts. of iodine, and the distillate repeatedly washed with water, digested with chloride of calcium, and rectified two or three times. (Cahours.) — 2. Four pts. of iodine are gradually dissolved in 7 pts. of pure fusel-oil, and a stick of phosphorus moved about in the liquid after each fresh addition of iodine, till it is completely decolorised; the oil, which gives off fumes of hydriodic acid in the air, distilled in the water-bath, till a thick, non-volatile, very acid liquid, insoluble in water, remains; the distillate, containing hydriodic acid and unaltered fusel-oil, washed with water, set aside for 24 hours over chloride of calcium, and rectified; and the last third, which passes over at 146°, collected as pure iodide of amyl. If the hydriodic acid has not been completely removed by the washing, the distillate is violet, but becomes colourless by rectifi-

cation over mercury. — The first two-thirds, which pass over between 120° and 146°, consist of impure iodide of amyl, and must be again treated with iodine and phosphorus. (Frankland.) — Grimm (*Ann. Pharm.* 92, 383) adds 10 oz. of iodine and a small quantity of phosphorus to 8 oz. of pure amylic alcohol. The amylic alcohol is mixed with 4 or 5 per cent. of water, and saturated with iodine; the solution, after being heated to 50°, shaken up with a small quantity (about $\frac{1}{4}$ of an ounce) of phosphorus till it is decolorised; again saturated with iodine and treated with phosphorus, and so on till the assigned quantity of iodine has been used: the liquid must be well cooled, as often as any rise of temperature takes place. The strongly fuming liquid ultimately obtained is distilled after standing for 24 hours; the distillate shaken up with water; iodine added in small quantities as long as its colour disappears; and the heavy liquid at the bottom re-distilled as before with water, then left to stand for a few days, and rectified.

*Properties.* Colourless liquid, heavier than water, boiling at 120°, under a pressure of 0·76 met.; of vapour-density 6·675; having an alliaceous odour and pungent taste. (Cahours.) Sp. gr. 1·511 at 11·5°; 1·4936 at 20° (Grimm); boiling point 146° at 0·75 met. pressure; 149° (Grimm.) Has a faint ethereal odour and sharp biting taste. (Frankland.)

| | | | Cahours. | Frankland. | Grimm. |
|---|---|---|---|---|---|
| 10 C | 60 | 30·46 | 31·00 | 30·32 | 30·5 |
| 11 H | 11 | 5·58 | 5·29 | 5·55 | 5·89 |
| I | 126 | 63·96 | .... | .... | 64·10 to 62·61 |
| $C^{10}H^{11}I$ | 197 | 100·00 | | | |

| | Vol. | Density. |
|---|---|---|
| C-vapour | 10 | 4·1600 |
| H-gas | 11 | 0·7623 |
| I-vapour | 1 | 8·7356 |
| Vap. of $C^{10}H^{11}I$ | 2 | 13·6579 |
| | 1 | 6·8289 |

*Decompositions.* 1. Iodide of amyl is not inflammable when cold, but when heated to its boiling point, may be set on fire by a flaming body, and burns with a purple flame. (Cahours.) — 2. It undergoes no change in ordinary day-light, but in sun-shine acquires a continually deepening yellow colour from separation of iodine; it may be rendered colourless again by potash. (Cahours.) It is but slowly decomposed by aqueous potash, even at a boiling heat, but quickly by alcoholic potash, so that iodide of potassium separates out on cooling. (Cahours.) — 4. Heated with zinc-amalgam in a sealed glass-tube, somewhat above its boiling point, it is resolved into $C^5H^5$ [$C^{10}H^{10}$, amylene], $C^5H^6$, [$C^{10}H^{12}$, hydride of amyl], $C^{10}H^{11}$ [$C^{20}H^{22}$] and iodide of zinc; the compound $C^{10}H^{11}Zn$ is likewise formed (Frankland);

$$[4C^{10}H^{11}I + 4\,Zn = C^{10}H^{10} + C^{10}H^{12} + C^{20}H^{22} + 4ZnI;$$

and :

$$C^{10}H^{11}I + 2Zn = C^{10}H^{11}Zn + ZnI.]$$

Pure zinc does not decompose iodide of amyl till heated to 190°, and then but slowly; potassium decomposes it very easily, even at its melting point, with formation of the same products, but not of $C^{10}H^{11}K$. (Frankland.)

— In presence of water, zinc decomposes iodide of amyl, even at 142°, and more quickly, into $C^5H^6$ [$C^{10}H^{12}$] and oxyiodide of zinc. (Frankland);

$$[C^{10}H^{11}I + HO + 2Zn = C^{10}H^{12} = ZnI,ZnO].$$

## Bromide of Amyl.

$$C^{10}H^{11}Br = C^{10}H^{10},HBr.$$

Cahours (1839). *Ann. Chim. Phys.* 70, 81; also *J. pr. Chem.* 17, 224.

*Bromamyl, bromwasserstoffsaures Amylen, Bromhydrate d'Amylene.*

Obtained by distilling fusel-oil with phosphorus and bromine, similarly to the iodide.

Transparent, colourless; heavier than water; distils without decomposition; has an alliaceous and pungent odour and a sharp taste:

| | | | | | Cahours. |
|---|---|---|---|---|---|
| 10 C | 60 | .... | 39·74 | ........ | 41·79 |
| 11 H | 11 | .... | 7·28 | ........ | 7·55 |
| Br | 80 | .... | 52·98 | | |
| $C^{10}H^{11}Br$ | 151 | .... | 100·00 | | |

| | Vol. | | Density. |
|---|---|---|---|
| C-vapour | 10 | .... | 4·1600 |
| H-gas | 11 | .... | 0·7623 |
| Br-vapour | 1 | .... | 5·5465 |
| Vap. of $C^{10}H^{11}Br$ | 2 | .... | 10·4688 |
| | | | 5·2344 |

Bromide of amyl is difficult to set on fire by a flaming body, and burns with a greenish flame. It is decomposed slowly by aqueous, quickly by alcoholic potash, with formation of bromide of potassium. It is not altered by exposure to sunshine. Dissolves in alcohol and ether. (Cahours.)

## Chloride of Amyl.

$$C^{10}H^{11}Cl = C^{10}H^{10},HCl.$$

Cahours (1840). *Ann. Chim. Phys.* 75, 193.
Balard. *N. Ann. Chim. Phys.* 12, 294; also *J. pr. Chem.* 34, 128.

*Chloramyl, Chlormylafer, Ether hydrochloramylique, Chlorhydrate d'Amylène.*

*Preparation.* 1. Fusel-oil is distilled with an equal weight of pentachloride of phosphorus, and the distillate repeatedly washed with water containing potash, dried over chloride of calcium, and finally rectified in a bath of salt-solution. (Cahours.) — 2. Fusel-oil is distilled with strong hydrochloric acid, with frequent cohobation; the resulting chloride of

amyl pipetted from the acid distillate; and freed from unaltered fusel-oil by washing with strong hydrochloric acid. (Balard.) — 3. Fusel oil is saturated in a tubulated retort with hydrochloric acid gas, whereupon it becomes heated and turns green; it is then distilled, the passage of the gas being continued all the while; and the amethyst-coloured distillate of chloride of amyl is washed with water and carbonate of soda, afterwards dried over chloride of calcium, and rectified. (Rieckher. *Jahrb. pr. Pharm.* 14, 1.)

*Properties.* — Colourless liquid, boiling at 102° (Cahours), between 100° and 101° according to Balard. Vapour-density 3·805. (Balard.) Has a tolerably pleasant aromatic odour; neutral; does not render silver-solution turbid. (Cahours.)

| | | | Cahours. | Balard. |
|---|---|---|---|---|
| 10 C | 60·0 | 56·39 | 56·06 | 55·9 |
| 11 H | 11·0 | 10·34 | 10·43 | 10·3 |
| Cl | 35·4 | 33·27 | 33·44 | 33·5 |
| $C^{10}H^{11}Cl$ | 106·4 | 100·00 | 99·93 | 99·7 |

| | Vol. | Density. |
|---|---|---|
| C-vapour | 10 | 4·1600 |
| H-gas | 11 | 0·7623 |
| Cl-gas | 1 | 2·4543 |
| Vapour of $C^{10}H^{11}Cl$ | 2 | 7·3766 |
| | 1 | 3·6883 |

Chloride of amyl burns with a green-bordered flame, giving off hydrochloric acid. (Cahours.) — Exposed to the sun in a bottle filled with dry chlorine gas, it is converted, first with quick and afterwards with decreasing evolution of hydrochloric acid, into $C^{10}H^3Cl^9$, a colourless liquid, which smells strongly of camphor, and would probably be completely converted into $C^{10}Cl^{12}$, if the action of the chlorine were longer continued. (Cahours.) — Heated to 100° in a sealed tube with alcoholic potash or with monosulphide of potassium, it is resolved into amylic ether and chloride of potassium, or into sulphide of amyl and chloride of potassium. (Balard.)

$$C^{10}H^{11}Cl + KO = C^{10}H^{11}O + KCl$$

and

$$C^{10}H^{11}Cl + KS = C^{10}H^{11}S + KCl.$$

Alcoholic potash and monosulphide of potassium do not act upon it in the cold. — When chloride of amyl is distilled with potash-lime, amylene distils over. (Balard.)

Chloride of amyl is insoluble in water. (Cahours.)

## Chloramylal.

CAHOURS. *Ann. Chim. Phys.* 70, 81; also *Ann. Pharm.* 30, 209.

When chlorine gas is passed through about 30 grammes of fusel-oil, absorption takes place at first, with formation of a large quantity of hydrochloric acid, the liquid turning brown and becoming heated to ebullition, so that it becomes necessary to cool it from without; but

afterwards the action becomes slow, and must be sustained by gentle heating, till the chlorine ceases to act. The resulting brown oil is repeatedly washed with water containing carbonate of soda, then digested over chloride of calcium, and rectified two or three times.

In this manner, a pale yellow oil is obtained, heavier than water, and boiling at about 180°; its vapour excites coughing when inhaled; it is tasteless at first, but leaves a very pungent after-taste.

The recently prepared alcoholic solution does not precipitate nitrate of silver, but on standing it turns acid and precipitates the silver.

Chloramylal is insoluble in water and in alkaline liquids, but dissolves in alcohol and ether. (Cahours.)

| | | | | | | |
|---|---|---|---|---|---|---|
| | | | | | | Chours. |
| 10 C | 60·0 | .... | 43·60 | ........ | | 44·23 |
| $1\frac{1}{2}$ Cl | 53·1 | .... | 38·59 | ........ | | 38·38 |
| $8\frac{1}{2}$ H | 8·5 | .... | 6·18 | ........ | | 6·05 |
| 2 O | 16·0 | .... | 11·63 | ........ | | 11·34 |
| | 137·6 | .... | 100·00 | ........ | | 100·00 |

Probably the action of the chlorine was not complete. (Cahours.) [Perhaps therefore $C^{10}Cl^2H^8,O^2$].

## ¶. Telluramyl. $C^{10}H^{11}Te$.

F. Wöhler & J. Dean. *Ann. Pharm.* 97, 1.

Obtained in an impure state by distilling telluride of potassium with a solution of amylosulphate of lime (prepared with amylic alcohol which passed over at 132° in the distillation of crude fusel-oil). As soon as the mixture began to boil, a reddish yellow liquid passed over with the water and sank to the bottom of it. The receiver was changed when the liquid which passed over began to exhibit a light colour; and at last colourless amylic alcohol distilled over.

The liquid thus obtained has an odour like that of tellurethyl and telluromethyl, but less strong and disagreeable. Exposed for some time to the air, it is converted into a white mass. The boiling point was found to be 198°; this determination is however quite uncertain, because the compound decomposes when heated, even in an atmosphere of carbonic acid, gradually depositing tellurium in small shining prisms.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | | | | | Wöhler & Dean. | | |
| 10 C | 60 | .... | 44·4 | ........ | 39·5 | .... | 38·3 |
| 11 H | 11 | .... | 8·1 | ........ | 7·4 | .... | 8·2 |
| Te | 64 | .... | 47·5 | ........ | 37·0 | .... | 35·4 |
| $C^{10}H^{11}Te$ | 135 | .... | 100·0 | ........ | 83·9 | .... | 81·9 |

The great differences between the analytical and calculated results are probably due to the presence of amylic alcohol separated by the decomposition above noticed. To remove this source of error, the body had been dissolved in warm weak nitric acid and reprecipitated with sulphite of ammonia; but this mode of purification was evidently ineffectual. The carbon and hydrogen found by analysis agree nearly with the formula of tellurobutyl $C^8H^9Te$, which requires 39·6 p.c. C, 7·4 H, and 53·0 Te; but the amount of tellurium obtained is much too small.

*Nitrate of Telluramyl.* — Telluramyl heated with moderately strong nitric acid, is converted, with evolution of nitric oxide gas, into a transparent, colourless, heavy oil, which appears to be the nitrate in the amorphous state. It dissolves in a large quantity of boiling water, and if the quantity of water has been rightly chosen, separates after a few days in thin rhombic tabular crystals. If the solution is too concentrated, it becomes milky on cooling, in consequence either of the salt again separating in the oily form, or else of another body separating out, in which the crystallisable salt remains dissolved. — Nitrate of telluramyl is permanent in the air, inodorous, and melts at 40°. When heated in the air, it burns with a blue tellurium-flame. Sulphurous acid throws down from its solution a yellowish red liquid having an offensive odour.

The nitrate gave by analysis 37·8 p. c. tellurium. The formula $C^{10}H^{11}TeO,NO^5$ requires 32·6 p. c. If the composition of the salt were analogous to that of the sulphate and oxalate of tellurethyl (viii, 385), viz., $C^{10}H^{11}TeO,HO + C^{10}H^{11}TeO,NO^5$, the amount of tellurium would be 36·9 p. c. The formula of nitrate of tellurobutyl requires 35 p. c. tellurium.

*Chloride of Telluramyl* is formed by mixing the solution of the nitrate with hydrochloric acid or chloride of sodium. Colourless, viscid, glutinous inodorous oil, heavier than water.

The *Bromide* is obtained in a similar manner, and is a pale-yellow heavy oil possessing similar properties.

The *Iodide* separates from the milky liquid at first produced, in the form of heavy, dark yellowish red, semifluid drops; it could not be obtained in the crystalline form. When boiled with alcohol, it was converted into a pale yellow, amorphous, inodorous powder, which, when treated with ammonia, acquired a vermilion colour, dissolved in the ammonia when heated, and separated out again with the vermilion colour on cooling. Nitric acid separated iodine from it.

*Oxide of Telluramyl* was obtained by digesting the chloride with silver-oxide and water: the viscid character of the chloride renders the decomposition very slow. The oxide is soluble in water, and so strongly alkaline, that it separates ammonia from sal-ammoniac. With hydrochloric acid it reproduces the oily chloride. Sulphurous acid reduces telluramyl from it in yellowish red, odorous, oily drops. — On neutralising the oxide with sulphuric acid, and evaporating the solution, it yielded, at a certain degree of concentration, colourless, viscid drops, which, after cooling gradually changed to groups of small prisms. (Wöhler & Dean.) ¶.

### *Conjugated Compounds of the Primary Nucleus* $C^{10}H^{10}$.

## Carbonate of Amyl.

$$C^{11}H^{11}O^3 = C^{10}H^{11}O,CO^2.$$

MEDLOCK (1849). *Chem. Soc. Qu. J.* 1, 363. *Ann. Pharm.* 69, 217.

*Kohlensaures Amyloxyd, Kohlenmylester.*

In the distillation of chloroformiate of amyl (p. 66), after carbonic and hydrochloric acid have gone off, and the boiling point has risen to

224° and become stationary there, carbonate of amyl passes over, and must be purified by further rectification.

Transparent liquid of sp. gr. 0·9144; boiling steadily at 224°, and having a not unpleasant odour.

| | | | | | Medlock. |
|---|---|---|---|---|---|
| 11 C | 66 | .... | 65·35 | ........ | 65·19 |
| 11 H | 11 | .... | 10·89 | ........ | 10·94 |
| 3 O | 24 | .... | 23·76 | ........ | 23·87 |
| $C^{11}H^{11}O^3$ | 101 | .... | 100·00 | ........ | 100·00 |

Carbonate of amyl is immediately decomposed by alcoholic potash, into amylic alcohol and carbonate of potash, which produces a thickening of the liquid. — With aqueous or alcoholic potash it does not form any compound of the nature of urethane. (Medlock.)

## Terbasic Borate of Amyl.

$C^{30}H^{33}BO^6 = 3C^{10}H^{11}O,BO^3$.

Ebelmen & Bouquet (1846). *N. Ann. Chim. Phys.* 17, 61; also *J. pr Chem.* 38, 219.

*Triborate of Amyl, Drittelborsaures Amyloxyd, Drittel-Bormylester, Protoborate amylique.*

*Preparation.* A mixture of chloride of boron and carbonic oxide is passed (as in the preparation of terbasic borate of ethyl, viii, 394), through fusel-oil, till hydrochloric acid begins to escape, and an oil rises to the top of the liquid saturated with hydrochloric acid; this oil is then decanted and rectified, the portion which distils over between 260° and 280° being collected apart and rectified again.

*Properties.* Colourless oil, of sp. gr. 0·870 at 0°. Boils between 270° and 275° and has a vapour-density of 10·55. Has a faint odour of fusel-oil.

| | | | | | Ebelmen & Bouquet. |
|---|---|---|---|---|---|
| 30 C | 180·0 | .... | 66·22 | ........ | 65·6 |
| 33 H | 33·0 | .... | 12·14 | ........ | 12·3 |
| 3 O | 24·0 | .... | 8·83 | | |
| $BO^3$ | 34·8 | .... | 12·81 | ........ | 11·9 |
| $C^{30}H^{33}O^3,BO^3$ | 271·8 | .... | 100·00 | | |

| | Vol. | | Density. |
|---|---|---|---|
| C-vapour | 30 | .... | 12·4800 |
| H-gas | 33 | .... | 2·2869 |
| B-vapour | 1 | .... | 0·7487 |
| O-gas | 3 | .... | 3·3279 |
| Vapour | 2 | .... | 18·8435 |
| | 1 | .... | 9·4217 |

This compound burns with a white green-edged flame, giving off vapours of boracic acid. — In contact with water, it is converted into boracic acid and fusel-oil. (Ebelmen & Bouquet.)

## Biborate of Amyl.

$C^{10}H^{11}B^2O^7 = C^{10}H^{11}O,2BO^3$.

EBELMEN (1846). *N. Ann. Chim. Phys.* 16, 139; also *Ann. Pharm.* 57 329; also *J. pr. Chem.* 37, 355.

*Zwerfuchborsaures Ameloxyd, Doppelt-Bormylester, Deutoborate amylique.*

*Formation and Preparation.* On mixing 2 pts. of fusel-oil with 1 pt. of vitrefied boracic acid in powder, a slight evolution of heat takes place, and the mixture yields scarcely any distillate at 180°, but if afterwards treated with anhydrous ether, gives up to it the borate of amyl, which remains behind on evaporating the filtrate, ultimately between 250° and 270°.

*Properties.* Like biborate of ethyl, yellowish, transparent; at 20°, it may be drawn out into long threads, like softened glass. Smells like fusel-oil and has a burning taste.

| | | | Ebelmen. |
|---|---|---|---|
| 10 C | 60·0 | 40·38 | 39·1 |
| 11 H | 11·0 | 7·40 | 7·3 |
| O | 8·0 | 5·38 | 8·6 |
| 2 $BO^3$ | 69·6 | 46·84 | 45·0 |
| $C^{10}H^{11}O,2BO^3$ | 148·6 | 100·00 | 100·0 |

Biborate of ethyl remains unaltered up to 300°; above 300°, it gives off white fumes in the air, then swells up and leaves fused boracic acid. — It burns with a green flame. — It is decomposed by water, and even by damp air, into boracic acid and fusel-oil. (Ebelmen.)

## Phosphite of Amyl.

$C^{20}H^{23}PO^6 = 2C^{10}H^{11}O,PHO^4$.

WURTZ (1845). *N. Ann. Chim. Phys.* 16, 221; also *Ann. Pharm.* 58, 75; abstr. *Compt. rend.* 21, 358.

*Phosphorig-Mylester, Amylphosphorsaures Amyloxyd, Ether amylophosphoreux.*

*Formation.* (p 15). — *Preparation.* 1 vol. terchloride of phosphorus is slowly dropped into 1 vol. fusel-oil, and a small quantity of water very slowly added, the vessel being well cooled, so that the product may not become coloured by the temperature rising too high. After all the excess of chloride of phosphorus has been decomposed by the water, the mixture is shaken up with an equal volume of water; the oily mixture of phosphite of amyl and amylophosphorous acid, which rises to the surface on leaving the liquid at rest, decanted; freed from hydrochloric acid by repeated washing with water, and from amylophosphorous acid by washing with dilute carbonate of soda, till the residual phosphite of amyl no longer reddens litmus; then washed twice with water; and heated several times in vacuo to 80°—100° to drive off water and chloride of amyl. Should the phosphite of amyl be coloured, it must be rectified in

vacuo; but this process is always attended with a certain amount of decomposition; for the distillate contains fusel-oil, and an acid residue is left.

*Properties.* Colourless or pale yellow oil, of sp. gr. 0·967 at 19°. Boils only at a high temperature and with some decomposition. Smells slightly of fusel-oil; has a very pungent and disagreeable taste.

| | | | Wurtz. |
|---|---|---|---|
| 20 C | 120·0 | 53·96 | 54·27 |
| 23 H | 23·0 | 10·34 | 10·38 |
| P | 31·4 | 14·12 | 12·55 |
| 6 O | 48·0 | 21·58 | 22·80 |
| $C^{20}H^{23}PO^6$ | 222·4 | 100·00 | 100·00 |

From admixture of fusel-oil or chloride of amyl, the quantity of carbon obtained was somewhat too large, and the phosphorus somewhat too small.

*Decompositions.* 1. Phosphite of amyl passed in the state of vapour through a red-hot tube, yields gases among which phosphuretted hydrogen occurs. — 2. It may be set on fire by a flaming body when strongly heated; paper soaked in it burns, when set on fire, with a white phosphorus flame. — 3. It absorbs chlorine gas, with rise of temperature and evolution of hydrochloric acid; in the dark at 0°, there is formed hereby a product containing 1 At. chlorine; but under the influence of heat and light, products very rich in chlorine are formed; these bodies are colourless and viscid, and decompose after a while, with evolution of hydrochloric acid. — 4. Nitric acid acts violently on phosphite of amyl, yellow oily drops passing over, and a strong odour of valerianic acid being evolved. — 5. When phosphite of amyl is boiled with solution of nitrate of silver, there is formed, with a certain amount of reduction, a black magma containing phosphate of silver. — 6. Exposed to moist air or kept in loosely closed vessels, it gradually turns acid. — 7. By boiling aqueous alkalis, it is quickly resolved into fusel-oil which passes over, and a residue of alkaline phosphite. (Wurtz.)

## Amylophosphorous Acid.

$$C^{10}H^{13}PO^6 = C^{10}H^{12}O^2,PHO^4.$$

WURTZ. *N. Ann. Chim. Phys.* 16, 227; also *Ann. Pharm.* 58, 75; abstr. *Compt. rend.* 21, 358.

*Amylphosphorige Säure, Acide amylophosphoreux.*

*Formation* (p. 15. — *Preparation.* After the oily mixture of phosphite of amyl and amylophosphorous acid has been freed from hydrochloric acid by washing with water (p. 47), the amylophosphorous acid is extracted from it by means of dilute carbonate of soda (a strong solution of that salt would likewise dissolve the phosphite of amyl); the alkaline solution separated mechanically from the phosphite of amyl which floats on the surface; the portion which still remains dissolved therein, separated by agitation with vinic ether; and the alkaline solution supersaturated with hydrochloric acid, whereby the amylophosphorous acid is

separated, with strong turbidity, and at first rises to the surface in the form of an oil, in consequence of containing vinic ether, but sinks to the bottom after the ether is evaporated. Lastly, to free this oil from chloride of sodium, it is dissolved in water, reprecipitated by hydrochloric acid, gently heated, after the aqueous hydrochloric acid has been decanted, and placed in a vacuum, to remove the water and hydrochloric acid.

*Properties.* Oil which sinks in water, nearly inodorous in the fresh state, but strongly acid.

| | | | Wurtz. |
|---|---|---|---|
| 10 C | 60·0 | 39·37 | 39·47 |
| 13 H | 13·0 | 8·53 | 8·55 |
| P | 31·4 | 20·60 | 19·72 |
| 6 O | 48·0 | 31·50 | 32·26 |
| $C^{10}H^{13}PO^6$ | 152·4 | 100·00 | 100·00 |

*Decompositions.* 1. The acid yields by dry distillation, a large quantity of combustible gas, and a small quantity of liquid distillate, leaving hydrated phosphorous acid, which, when more strongly heated, gives off phosphuretted hydrogen gas. — 2. Amylophosphorous acid burns with a very smoky flame and leaves the hydrate of phosphorous acid. — 3. It reduces silver-salts. — 4. After being kept for some time, it no longer dissolves completely in water, and the solution quickly decomposes into fusel-oil and phosphorous acid. The acid separated by hydrochloric acid from the soda-salt which has been kept for some time, likewise exhibits this behaviour.

*Combinations.* Dissolves readily in *water*, and is precipitated there from by hydrochloric acid.

Decomposes the alkaline carbonates with effervescence. Its salts decompose readily.

The *potash-* and *soda-salts* can only be obtained in the gelatinous state.

The *baryta-salt* dries up in vacuo to a soft deliquescent mass.

The *lead-salt* is a white curdy precipitate, which decomposes even in the dry state, and quickly when moist, giving off an odour of fusel-oil. (Wurtz.)

## ¶. Amylophosphoric Acid.

$$C^{10}H^{13}PO^8 = C^{10}H^{12}O^2,PHO^6.$$

FREDERICK GUTHRIE. *Chem. Soc. Qu. J.* 9, 134; *Ann. Pharm.* 99, 57.

*Formation and Preparation.* When equal weights of amylic alcohol and syrupy phosphoric acid are shaken up together in a flask, till perfect mixture takes place, they unite, producing considerable rise of temperature, and the mass assumes a pale red colour. On leaving the mixture to stand for 24 hours at 60° to 80°, the colour changes to a deep wine red and amylophosphoric acid is formed. The acid liquid is then shaken up with warm water, which dissolves the amylophosphoric and a certain quantity of free phosphoric acid, leaving the uncombined fusel-oil undissolved; the several aqueous solutions united, slightly supersaturated with

carbonate of potash, and evaporated nearly to dryness in the water-bath; the residual mass, consisting of amylophosphate, phosphate, and carbonate of potash, digested with warm alcohol to separate the two latter salts, and quickly filtered; the solution, which contains all the amylophosphate together with a small quantity of phosphate, again evaporated nearly to dryness; the residue again exhausted with alcohol; and this operation several times repeated with continually stronger, and at last with absolute alcohol. The amylophosphate of potash may be regarded as pure [free from phosphate], when a sample dissolved in water gives a snow-white precipitate with nitrate of silver. The residue obtained by evaporating the alcoholic solution, is a yellowish transparent, gelatinous mass still containing amylic alcohol, to remove which impurity, the salt must be dissolved in water, the solution evaporated to dryness over the water-bath, and this treatment repeated once or twice. A tenacious honey-coloured mass is thus obtained consisting of minute crystals of pure amylophosphate of potash.

To obtain the free acid, the dilute solution of the potash-salt is precipitated with sulphate of copper; the well-washed and still moist precipitate suspended in water and decomposed by sulphuretted hydrogen; and the strongly acid liquid filtered as quickly as possible and evaporated to a syrup over the water-bath. At this stage of concentration, the acid suffers no further loss of weight when placed over sulphuric acid. When it is replaced on the water-bath, minute crystals are formed, which under the microscope appear to be long needles.

*Properties.* Amylophosphoric acid is inodorous, has a strong acid taste and expels carbonic acid from its salts. It is much more stable than ethylophosphoric acid, inasmuch as it bears the heat of the water-bath without decomposition, the syrupy acid prepared as above, giving, when dissolved in water and neutralized with ammonia, a perfectly white precipitate with nitrate of silver. Heated in the flame of a lamp, it burns with a white flame, leaving a residue of phosphoric acid.

*Combinations.* The acid is soluble in *water.* The crystallised acid absorbs moisture eagerly from the air, and deliquesces.

The formula of the *Amylophosphates* is $C^{10}H^{11}M^2PO^8 = C^{10}(H^{10}M^2)O^2, PHO^6 = 2MO, C^{10}H^{11}O,PO^5$.— The amylophosphates of the alkalies are soluble in water; the rest insoluble or sparingly soluble. They are, in general, more soluble than the corresponding terbasic phosphates. They all dissolve readily in nitric or hydrochloric acid. They are generally speaking, more stable than the corresponding ethylophosphates and ethylosulphates, inasmuch as they bear the heat of boiling water without decomposition.

When an electric current (from 4 Bunsen's cells) was passed through a concentrated solution of amylophosphate of potash, separated into two portions by a clay partition, the electrodes being of platinum, hydrogen was liberated at the negative, and oxygen together with carbonic acid at the positive pole. The solution at the positive pole assumed an acid reaction, and smelt distinctly of valerianic or butyric acid (secondary products of decomposition). The liquid at the negative pole became alkaline, but remained odourless, showing that no amyl-compound was there eliminated. From this experiment, and from similar results obtained with the amylosulphates and sulphovinates, Guthrie concludes that we are not at liberty to assume (as is commonly done) that the

organic oxides in these and similar salts are combined in the same manner as the metallic oxides, but rather that the acid together with the organic oxide forms a conjugated acid : *e. g.* in the amylophosphates : the phosphoric acid with the oxide of amyl forms a bibasic amylophosphoric acid.

*Amylophosphate of Ammonia.* $2NH^4O, C^{10}H^{11}O, PO^5$.—Obtained by decomposing the freshly precipitated copper salt suspended in water, with sulphide of ammonium, boiling the filtrate, filtering again, evaporating to dryness over the water-bath, and recrystallising from alcohol to remove sulphite and sulphate of ammonia formed during the reaction. Also, and in a state of greater purity, by neutralising amylophosphoric acid with ammonia. — Resembles the potash-salt.

*Amylophosphate of Potash.* $2KO, C^{10}H^{11}O, PO^5$. — (*Preparation* *p.* 50). Tenacious, finely crystallised, translucent salt, without odour, but having the well-known taste peculiar to amyl-compounds. When exposed to the air, it absorbs moisture and deliquesces to a syrupy transparent liquid having a faint odour. Dried as completely as possible and then heated in a tube by itself, it yields fusel-oil. Heated on platinum-foil in the flame of a lamp, it intumesces considerably, probably from escape of water, and then burns with a pure white flame, leaving a residue of pyrophosphate of potash. Dissolves in all proportions in water either hot or cold; soluble also in alcohol, but insoluble in ether.

*Amylophosphate of Baryta.*— Precipitated from a solution of the potash-salt, on addition of chloride of barium, in white scales having a silky lustre. From cold solutions, the precipitation is slow, but is accelerated by heat, which more especially favours the formation of the scales. It collects chiefly on the surface of the liquid, probably in consequence of its fatty nature.

| | | | Guthrie. |
|---|---|---|---|
| 2 Ba | 137·2 | 45·19 | 44·63 |
| 10 C | 60·0 | 19·76 | 19·00 |
| 11 H | 11·0 | 3·62 | 4·24 |
| $PO^5$ | 71·4 | 23·52 | 23·45 |
| 3 O | 24·0 | 7·91 | 8·68 |
| $2BaO, C^{10}H^{11}O, PO^5$ | 303·6 | 100·00 | 100·00 |

*Amylophosphate of Lead.*— Precipitated from a dilute solution of the potash-salt, on addition of acetate of lead. The precipitate, after washing and drying at 100°, is a bulky, white, anhydrous powder, without taste or smell. Dissolves readily in hydrochloric and acetic acids.

| | | | Guthrie. |
|---|---|---|---|
| 2 Pb | 208·0 | 55·55 | 56·4 |
| 10 C | 60·0 | 16·03 | 15·5 |
| 11 H | 11·0 | 2·94 | 3·2 |
| $PO^5$ | 71·4 | 19·07 | 20·3 |
| 3 O | 24·0 | 6·41 | 4·6 |
| $2PbO, C^{10}H^{11}O, PO^5$ | 374·4 | 100·00 | 100·0 |

*Amylophosphate of Copper.*— Precipitated on adding a dilute solution of sulphate of copper, to a dilute solution of amylophosphate of potash.

The precipitate is at first almost white, but gradually assumes a bluish tinge, and in the dry state is a light blue amorphous powder. Bears a heat of 110° without decomposing.

| | | | Guthrie. |
|---|---|---|---|
| 2 Cu | 64·0 | 27·78 | 28·1 |
| 10 C | 60·0 | 26·04 | 25·6 |
| 11 H | 11·0 | 4·77 | 4·8 |
| $PO^5$ | 71·4 | 30·99 | 30·4 |
| 3 O | 24·0 | 10·42 | 11·1 |
| $2CuO,C^{10}H^{11}O,PO^5$ | 230·4 | 100·00 | 100·0 |

In a solution of *mercurous nitrate,* amylophosphate of potash produces a precipitate in the form of a white amorphous powder.

*Amylophosphate of Silver.*— Obtained as a white bulky precipitate on adding nitrate of silver to a solution of the potash-salt. Turns grey when exposed to light, but remains white in the dark. Appreciably soluble in warm water, but does not separate in the crystalline form on cooling. Decomposed by long boiling with water, silver being deposited. Heated on platinum-foil, it turns yellow, and leaves pyrophosphate of silver.

| | | | Guthrie. |
|---|---|---|---|
| 2 Ag | 206·0 | 56·48 | 56·14 |
| 10 C | 60·0 | 15·69 | 15·28 |
| 11 H | 11·0 | 2·88 | 3·29 |
| $PO^5$ | 71·4 | 18·67 | 18·21 |
| 3 O | 24·0 | 6·28 | 7·08 |
| $2\,AgO,C^{10}H^{11}O,PO^5$ | 382·4 | 100·00 | 100·00 |

When dry amylophosphate of silver is introduced into a tube, and moistened with a few drops of chloride of amyl, the tube then sealed and heated for several hours to about 180°, decomposition ensues, chloride of silver being formed, together with an ethereal liquid, which may be dissolved out by alcohol, and precipitated therefrom in oily drops by addition of water. This oily liquid has an odour quite distinct from that of fusel-oil, and is probably the amylophosphate of oxide of amyl [terbasic phosphate of amyl], its formation being represented by the equation :

$$2AgO,C^{10}H^{11}O,PO^5 + 2C^{10}H^{11}Cl = 3C^{10}H^{11}O,PO^5 + 2AgCl.$$

Amylophosphoric acid dissolves in *alcohol,* but is insoluble in ether, so that it is precipitated by ether from its concentrated alcoholic solution. (Guthrie) ¶.

## Amylosulphurous Acid.

$$C^{10}H^{12}S^2O^6 \doteq C^{10}H^{12}O^2,2SO^2.$$

ERDMANN & GERATHEWOHL (1845). *J. pr. Chem.* 34, 447.
MEDLOCK. *Ann. Pharm.* 69, 224.

*Amylschweflige Säure, Sulfamylschwefelsäure* (Erdmann & Gerathewohl), *Hyposulphamylic acid, Amylunterschwefelsäure* (Medlock), *Acide sulfoamylolique.*

*Formation.* The chief product of the action of nitric acid on amyl-mercaptan (Erdmann & Gerathewohl), or on sulphocyanide of amyl (Medlock), or on bisulphide of amyl. (Henry.)

*Preparation.* 1. Nitric acid of sp. gr. 1·25 is gently heated in a tubulated retort, and amylmercaptan added to it, very gradually and in small portions, so that the mixture may not become too strongly heated, and no amylmercaptan may pass over undecomposed with the nitrous vapours,— the action being continued so long as any signs of oxidation appear on heating. The acid layer at the bottom of the retort, consisting of amylosulphurous, nitric, and a small quantity of sulphuric acid, is then separated from the supernatant oily liquid, and evaporated over the water-bath till the odour of nitrous and nitric acid is no longer perceptible; the remaining transparent and colourless syrup,— which consists of amylosulphurous acid contaminated with a little sulphuric acid, and may be used for the preparation of most of the amylosulphites (since these salts are soluble in alcohol, whereas the sulphites are insoluble) — diluted with water; the solution saturated with carbonate of lead, and filtered from the sulphate; and the filtrate treated with sulphuretted hydrogen, again filtered, and evaporated to a syrup over the water-bath. (Erdmann & Gerathewohl.) — 2. A mixture of equal parts of sulphocyanide of amyl and moderately strong nitric acid is gently heated in a retort, after the first violent action has subsided, with cohobation, and occasional addition of nitric acid, till the last traces of the sulphocyanide have disappeared; the liquid which remains in the retort evaporated in a basin over the water-bath; the remaining red liquid dissolved in water and again evaporated to expel the last traces of nitric acid; the residual nearly colourless liquid, which contains a little sulphuric acid, diluted with water and saturated with carbonate of lead, the filtrate evaporated till it crystallizes; the crystals dissolved in water; the lead precipitated by sulphuretted hydrogen; and the filtrate evaporated over the water-bath. (Medlock.)

*Properties.* Transparent, colourless syrup, having a peculiar odour and very sour taste, and not yielding crystals even in vacuo over oil of vitriol. (Erdmann & Gerathewohl). Gradually solidifies in vacuo over oil of vitriol to a crystalline mass. (Medlock.)

*Decomposition.* The acid chars when heated, emitting a very repulsive odour. (Medlock.)

*Combinations.* The acid absorbs water from the air (Erdmann & Gerathewohl), and deliquesces. (Medlock.)

The *Amylosulphites* (or *Sulfoamylolates*) are obtained, either by saturating the aqueous acid with the base or its carbonate, or by precipitating the baryta-salt with the sulphate of the corresponding base. They crystallise readily, and in external appearance resemble the etholysulphites. (Erdmann & Gerathewohl.) Their formula is $C^{10}H^{11}MO^2,2SO^2$.

The *Ammonia-salt* and the *Potash-salt*, crystallise in laminæ, and dissolve readily in water and alcohol. (Erdmann & Gerathewohl.)

*Amylosulphite of Baryta.* — The filtered solution of carbonate of baryta in the acid is evaporated over the water-bath (or better, spontaneously, according to Medlock).—Transparent, colourless laminæ, unctuous to the touch (having a pearly lustre, according to Medlock). They give off water at 100°, do not decompose at 160°, and burn with a bluish sulphur-flame at a stronger heat. (Erdmann & Gerathewohl.) They are anhydrous, and therefore suffer only a trifling loss at 100°.

(Medlock.) They move about on water like butyrate of baryta; dissolve in 10 pts. of water at 19°, in a smaller quantity of hot water, and likewise in alcohol. (Erdmann & Gerathewohl.) They dissolve very readily in water and alcohol. (Medlock.)

| | | | | | Erdmann & Gerathewohl. | | Medlock. |
|---|---|---|---|---|---|---|---|
| 10 C | 60·0 | .... | 27·32 | ........ | 26·92 | .... | 27·46 |
| 11 H | 11·0 | .... | 5·01 | ........ | 5·03 | .... | 5·22 |
| Ba | 68·6 | .... | 31·24 | ........ | 31·31 | .... | 31·11 |
| 2 S | 32·0 | .... | 14·57 | ........ | 15·33 | | |
| 6 O | 48·0 | .... | 21·86 | ........ | 21·41 | | |
| $C^{10}H^{11}BaO^2,2SO^2$ | 219·6 | .... | 100·00 | ........ | 100·00 | | |

*Amylosulphite of Lime.* — Colourless laminæ, easily soluble in water and alcohol. (Erdmann & Gerathewohl.)

*Amylosulphite of Lead.* — The salt purified by recrystallisation from alcohol, forms colourless laminæ united in radiated groups, which give off 23·48 p. c. [8 At.] water at 120°, turn brown at a stronger heat, giving off vapours having an exceedingly offensive odour and finally burn away with bluish sulphur-flame. (Erdmann & Gerathewohl.) The aqueous solution yields by spontaneous evaporation, anhydrous silky needles, which when heated give off an extremely offensive odour and leave sulphide of lead. (Medlock.) The salt dissolves very readily in water (Medlock), and so abundantly in hot alcohol, that the solution solidifies completely on cooling. (Erdmann & Gerathewohl.)

| | | | | | Erdmann & Gerathewohl, *at* 100° *in vacuo.* | | Medlock, *air-dried crystals.* |
|---|---|---|---|---|---|---|---|
| 10 C | 60 | .... | 23·53 | ........ | 24·02 | ........ | 23·65 |
| 11 H | 11 | .... | 4·32 | ........ | 4·64 | ........ | 4·23 |
| Pb | 104 | .... | 40·78 | ........ | 40·58 | ........ | 40·67 |
| 2 S | 32 | .... | 12·55 | | | | |
| 6 O | 48 | .... | 18·82 | | | | |
| $C^{10}H^{11}PbS^2O^6$ | 255 | .... | 100·00 | | | | |

*Cupric Amylosulphite.* — Blue green tables which, when placed over oil of vitriol, even at ordinary temperatures, give off water and become opaque. (Erdmann & Gerathewohl.) When the acid saturated with carbonate of copper, is evaporated to dryness over the water-bath, the residue extracted with alcohol, and the filtrate left to evaporate spontaneously in a narrow vessel, anhydrous crystalline laminæ are obtained. (Medlock.)

| *Crystals.* | | | | | Medlock. |
|---|---|---|---|---|---|
| 10 C | 60 | .... | 32·80 | ........ | 32·64 |
| 11 H | 11 | .... | 6·01 | ........ | 6·16 |
| Cu | 32 | .... | 17·48 | ........ | 17·33 |
| 2 S | 32 | .... | 17·48 | | |
| 6 O | 48 | .... | 26·23 | | |
| $C^{10}H^{11}CuS^2O^6$ | 183 | .... | 100·00 | | |

*Amylosulphite of Silver.* — The acid saturated with carbonate of silver, yields, if not too much evaporated, transparent, colourless, rhombic tables;

but, if too much concentrated, it solidifies to an amorphous jelly, like coagulated white of egg, and appearing under the microscope to consist of fine interlaced hairs. (Erdmann & Gerathewohl.)

| | At 100°. | | | Erdmann & Gerathewohl. |
|---|---|---|---|---|
| 10 C | 60 | .... | 23·16 | ........ 21·28 |
| 11 H | 11 | .... | 4·25 | ........ 3·99 |
| Ag | 108 | .... | 41·70 | ........ 43·89 |
| 2 S | 32 | .... | 12·36 | |
| 6 O | 48 | .... | 18·53 | |
| $C^{10}H^{11}AgS^2O^6$ | 259 | .... | 100·00 | |

Danson (*Chem. Soc. Qu. J.* 3, 158) prepares amylosulphurous acid from bisulphide of amyl and nitric acid.

## Amylosulphuric Acid.

$$C^{10}H^{12}S^2O^8 = C^{10}H^{12}O^2,SO^3.$$

Cahours (1839). *Ann. Chim. Phys.* 70, 86; also *J. pr. Chem.* 17, 216.
Kekulé. *Ann. Pharm.* 75, 275.

*Sulphamylic acid, Amylschwefelsäure.*

*Preparation.* A mixture of equal parts of fusel-oil and oil of vitriol (after standing for some time, till water no longer separates fusel-oil from it; *Kekulé*) is diluted with water; the resulting *crude amylosulphuric* acid saturated with carbonate of baryta; the solution filtered from the sulphate of baryta and evaporated; and the crystals of amylosulphate of baryta which separate after cooling, are freed from the mother-liquor upon blotting paper, and purified by shaking up their aqueous solution with animal charcoal, and twice crystallising by spontaneous evaporation. The solution of these crystals, precipitated by the proper quantity of sulphuric acid, then filtered and evaporated, yields the pure acid. (Cahours.)—Kekulé prefers preparing the lead-salt and decomposing it with sulpheretted hydrogen, after which he carefully evaporates the colourless filtrate to a thin syrup.

*Properties.* Colourless, thin syrup which sometimes deposits slender needles by spontaneous evaporation. (Kekulé did not obtain any crystals.) Tastes acid and bitter (sharply acid, according to Kekulé), and reddens litmus strongly. (Cahours.)

*Decompositions.* 1. The concentrated aqueous acid decomposes spontaneously into fusel-oil and sulphuric acid, slowly in the cold and in vacuo (or when exposed to the air; *Kekulé*), quickly on boiling (Cahours), the more quickly as it is more concentrated. (Kekulé.) — 2. It is decomposed by chlorine in the cold, and by nitric acid when heated. (Kekulé.)

*Combinations.* The acid dissolves very readily in *water*. (Cahours.) The *Amylosulphates* or *Sulphamylates* are for the most part =

$C^{10}H^{11}MO^2,2SO^3$. (Cahours). They are generally crystallisable, have a bitter taste, and are soapy to the touch. The crystals generally contain water and in that case are often efflorescent. (Kekulé.) When their aqueous solution is boiled, they are resolved into sulphate, free sulphuric acid and fusel-oil. (Cahours.) This decomposition takes place slowly at ordinary temperatures, even in the crystallised salts; nevertheless, these crystallised salts may generally be dehydrated at 100° before decomposition begins. (Kekulé.) For the decomposition by dry distillation see the lime-salt. All amylosulphates dissolve in water (Cahours), and in alcohol, very sparingly in ether. (Kekulé.)

*Amylosulphate of Ammonia.* — The filtrate obtained by precipitating the lime-salt with carbonate of ammonia, yields by spontaneous evaporation, colourless, bitter crystalline scales, and by evaporation over the water-bath, a nodular crystalline mass. The crystals give off nothing at 100°, begin to decompose at 140°, and burn away leaving a residue of charcoal. They deliquesce slightly in damp air, and dissolve very readily in water, on which they move briskly about; they are less soluble in alcohol, and insoluble in ether. (Kekulé.)

| *Crystals.* | | | Kekulé. |
|---|---|---|---|
| 10 C | 60 | 32·43 | 32·36 |
| N | 14 | 7·57 | |
| 15 H | 15 | 8·11 | 8·33 |
| 2 O | 16 | 8·65 | |
| 2 $SO^3$ | 80 | 43·24 | |
| $C^{10}H^{11}(NH^4)O^2,2SO^3$ | 185 | 100·00 | |

*Amylosulphate of Potash.* — The solution yields by spontaneous evaporation, colourless tufts of needles, having a very bitter taste (Cahours), or, nodules composed of needles having a silky lustre. (Kekulé.) These crystals effloresce on exposure to the air, and turn slightly brown, giving off fusel-oil and sulphuric acid. In vacuo or at 100°, they give off 3·99 per cent. (1 At.) of water, without further decomposition, swell up strongly at 170°, then melt, and leave a black scum. (Kekulé.) The salt dissolves readily in water and in weak alcohol (Cahours), less readily in strong alcohol, from the hot solution in which it crystallises in slender needles, and is insoluble in ether. (Kekulé.)

| *Dried in vacuo.* | | | Cahours. | Kekulé. |
|---|---|---|---|---|
| 10 C | 60·4 | 29·10 | 29·39 | |
| 11 H | 11·0 | 5·33 | 5·13 | |
| O | 8·0 | 3·88 | 3·89 | |
| $KO,SO^3$ | 87·2 | 42·29 | 42·21 | 42·39 |
| $SO^3$ | 40·0 | 19·40 | 19·38 | |
| $C^{10}H^{11}KO^2,2SO^3$ | 206·6 | 100·00 | 100·00 | |

*Amylosulphate of Soda.* — By precipitating the lime-salt with carbonate of soda and spontaneous evaporation of the bitter filtrate, nodules are obtained set with small crystals. These swell up at 35° [135?] softening, and giving off water, and begin to undergo further decomposition at 145°. They dissolve abundantly in cold water and in all proportions in hot water; from hot alcohol they crystallise in long radiated laminæ; they do not dissolve in ether. (Kekulé.)

| Crystals dried between paper. | | | | | Kekulé. |
|---|---|---|---|---|---|
| $C^{10}H^{11}O$ | 79·0 | .... | 36 38 | | |
| $NaO,SO^3$ | 71·2 | .... | 32·78 | ........ | 32·82 |
| $SO^3$ | 40·0 | .... | 18·42 | | |
| 3 HO | 27·0 | .... | 12·42 | ........ | 12·19 |
| $C^{10}H^{11}NaO^2,2SO^3 + 3Aq$ | 217·2 | .... | 100·00 | | |

*Amylosulphate of Baryta.* — *Preparation* (p. 55). — On the surface of the acid neutralised with carbonate of baryta and filtered, there generally floats a brown oil, which, after evaporation, may be separated by evaporation through a wet filter; any accidental colouring of the filtrate is easily removed by agitation with charcoal. (Kekulé.) — Laminæ having a strong pearly lustre and very bitter taste (Cahours), or, by spontaneous evaporation, large, very flexible, rhombic tables. (Kekulé.) The crystals effloresce in dry air and gives off 6·66 p. c. (the 1 At.) water in vacuo. They begin to decompose at 95°, melting at the same time, if they have not been previously dried. (Kekulé.) They give off an oil somewhat above 200°, and leave sulphate of baryta mixed with charcoal. Their aqueous solution is resolved by longer boiling, into fusel-oil, sulphuric acid, and sulphate of baryta. They dissolve very readily in water, more readily in warm than in cold alcohol, but are insoluble in ether. (Cahours.)

| Crystals dehydrated at 100°. | | | | | Cahours, at 100°. | | Medlock, cold in vacuo. |
|---|---|---|---|---|---|---|---|
| 10 C | 60·0 | .... | 24·53 | .... | 24·36 | | |
| 12 H | 12·0 | .... | 4·91 | .... | 4·93 | | |
| 2 O | 16·0 | .... | 6·54 | .... | 6·86 | | |
| $BaOSO^3$ | 116·6 | .... | 47·67 | .... | 47·45 | .... | 47·43 |
| $SO^3$ | 40·0 | .... | 16·35 | .... | 16·40 | | |
| $C^{10}H^{11}BaO^2,2SO^3 + Aq$ | 244·6 | .... | 100·00 | .... | 100·00 | | |

| Air-dried crystals. | | | | | Kekulé. |
|---|---|---|---|---|---|
| 10 C | 60·0 | .... | 23·65 | | |
| 13 H | 13·0 | .... | 5.13 | | |
| 3 O | 24·0 | .... | 9·45 | | |
| $BaO,SO^3$ | 116·6 | .... | 45·98 | .... | 45·93 |
| $SO^3$ | 40·0 | .... | 15·78 | | |
| $C^{10}H^{11}BaO^2,2SO^3 + 2Aq$ | 253·6 | .... | 100·00 | | |

*Amylosulphate of Strontia.* — White crystallised nodules, which turn brown in the air; leave 39·82 p. c. sulphate of strontia when ignited, and therefore contain 2 At. water; dissolve readily in water and weak alcohol, with difficulty in absolute alcohol, and not at all in ether. (Kekulé.)

*Amylosulphate of Lime.* — The crude acid is saturated, first, to avoid unnecessary effervescence, with hydrate of lime, which however must not be added in excess, and afterwards with chalk; the evaporated filtrate mixed with alcohol to precipitate the whole of the gypsum; and again filtered and evaporated. (Kekulé.) — White crystalline nodules, greasy to the touch and having a bitter and slightly pungent taste. (Cahours.) — The crystals effloresce in dry air and give off 8·55 p. c. (2 At.) water in vacuo. When kept for some time or heated in the water-bath, they slowly give off fusel-oil. When gradually heated from 100° to 150°, they turn soft and blacken, and give off first, sulphurous acid, a small quantity of carbonic acid, and a combustible vapour, and lastly more carbonic acid, together

with sulphur, while sulphate of lime and charcoal remain behind. The combustible vapour condenses to an oily mixture (contaminated with a sulphur-compound) of amylene $C^{10}H^{10}$, and amylic ether $C^{10}H^{11}O$, which increases in the course of the distillation. — By repeated fractional distillation of this oily mixture, the more volatile *amylene* is obtained in the form of a colourless oil, which floats on water, boils steadily at 42°, has a vapour-density of 2·4271, is tasteless, but has a slight smell of onions arising from the admixed sulphur-compound. It contains 83·50 p. c. C and 14·55 H. — The amylic ether, which is likewise contaminated with a sulphur-compound, does not exhibit any constant boiling point, and is partially decomposed at each rectification, the residue turning brown. The portion which distils over between 165° and 175°, contains 73·96 p. c. C 13·54 H and 12·50 O. Cold nitric acid forms with it a purple mixture without decomposition: and oil of vitriol forms a red syrup, from both of which, water again separates the colourless oil. (Kekulé.) — ¶. Amylosulphate of lime mixed with alcoholic ammonia and heated to 250° for two hours in a sealed tube, yields a mass which when distilled with potash gives off amylamine.

$$C^{10}H^{11}CaO^2,2SO^3 + NH^3 = \underbrace{C^{10}NH^{13},SHO^4}_{\text{sulphate of amylamine.}} + CaSO^4.$$

Sulphovinate of baryta heated in a similar manner with ammonia appears to give off ethylamine. (Berthelot, *Compt. rend.* 36, 1098. ¶.)—Amylosulphate of lime dissolves readily in cold, less readily in hot water, whence a solution saturated in the cold, becomes turbid on boiling. (Cahours.) [From the presence of gypsum ?]. The hot aqueous solution solidifies on cooling; it effloresces strongly when evaporated. The salt does not dissolve in hot alcohol more readily than in cold; it does not dissolve in ether. (Kekulé.)

| | *Air-dried crystals.* | | Cahours. |
|---|---|---|---|
| 10 C | 60 | 30·62 | 31·00 |
| 12 H | 12 | 6·12 | 6·00 |
| 2 O | 16 | 8·16 | 8·12 |
| CaO,$SO^3$ | 68 | 34·69 | 34·63 |
| $SO^3$ | 40 | 20·41 | 20·25 |
| $C^{10}H^{11}CaO,2SO^3$ + Aq | 196 | 100·00 | 100·00 |

According to Kekulé, the recently prepared crystals contain 2 At. water (*vid. sup.*)

*Amylosulphate of Magnesia.*—The solution of carbonate of magnesia in the pure aqueous acid, yields by spontaneous evaporation, transparent, colourless, nacreous, elongated, rhombic laminæ, which are with difficulty deprived of the whole of their 4 At. water, leave 28·2 p. c. sulphate of magnesia when ignited in the air, and dissolve in water and alcohol, but not in ether. (Kekulé.)

*Amylosulphate of Alumina.*—The colourless acid solution of hydrate of alumina in the acid, leaves, when evaporated in vacuo over oil of vitriol, a bitter jelly, which soon decomposes on standing, quickly deliquesces in a damp atmosphere, dissolves also in alcohol and ether. (Kekulé.)

*Amylosulphate of Manganese*—The pale red solution of carbonate of manganese in the pure acid, yields in vacuo, nearly colourless, transparent needles, permanent in the air. These crystals ignited in contact with air, leave 32·82 p. c. sulphate of manganese, and therefore contain 4 At. water. Their aqueous solution exposed to the air, slowly deposits brown nodules which precipitate chloride of barium. The needles dissolve also in alcohol but are insoluble in ether. (Kekulé.)

*Amylosulphate of Zinc.* The solution of carbonate of zinc in the acid deposits on evaporation nacreous laminæ, which decompose at 110°, and dissolve in water and in alcohol. (Kekulé.)

| *Crystals dried between paper.* | | | Kekulé. |
|---|---|---|---|
| $C^{10}H^{11}O,2SO^3$ | 159·0 | 73·20 | |
| ZnO | 40·2 | 18·51 | 18·50 |
| 2 HO | 18·0 | 8·29 | 8·49 |
| $C^{10}H^{11}ZnO^2,2SO^3 + 2Aq$ | 217·2 | 100·00 | |

*Amylosulphate of Lead.*—*a Bibasic.* The aqueous acid or the lead salt *b* is saturated by digestion with oxide of lead. The colourless neutral filtrate deposits small crystals; when quickly evaporated, it leaves a colourless viscid mass; when exposed to the air, it becomes covered with a film of carbonate of lead, and passes into the salt *b.* (Kekulé.)

*b. Monobasic.*—Obtained by dissolving carbonate of lead in the acid. (Cahours.) By carefully evaporating the filtered solution of white lead in the crude acid, ultimately over oil of vitriol at ordinary temperatures. (Kekulé.)—White laminæ having a sweet and somewhat bitter taste (Cahours); colourless, bitter-sweet, crystalline nodules, which redden litmus. (Kekulé.) The crystals dried between paper, leave, when ignited in the air, 52·32 p. c. (54·91, according to Kekulé) of sulphate of lead; they are therefore = $C^{10}H^{11}PbO^2,2SO^3 + Aq.$ (Cahours.) The aqueous solution deposits sulphate of lead, slowly when kept, quickly on boiling. (Cahours.) The salt dissolves very readily in water (Cahours), readily in alcohol, but is insoluble in ether. (Kekulé.)

*Ferrous Amylosulphate.*—The aqueous acid in contact with iron, gives off hydrogen, and forms a pale green, sweetish bitter solution which reddens litmus, and when evaporated, deposits brown flakes of ferric oxide, and deposits pale green crystalline grains. These crystals quickly turn yellow on exposure to the air, dissolve in water and alcohol, and with green colour in ether. (Kekulé.)

*Ferric Amylosulphate.*—The yellow solution of ferric hydrate in the acid, yields, on evaporation, small yellow, easily decomposible, deliquescent, crystalline granules. (Kekulé.)

*Amylosulphate of Cobalt.*—By precipitating the baryta-salt with sulphate of cobalt, and evaporating the filtrate, rose-coloured laminæ are obtained very soluble in water. (Cahours.)

*Amylosulphate of Nickel.*—The solution of the hydrated oxide in the acid, yields by evaporation, green elongated laminæ united in nodules, which deliquesce in moist air, dissolve in water and alcohol, but are

insoluble in ether. They contain 17·2 p. c. oxide of nickel, and therefore 2 At. water. (Kekulé.)

*Cupric Amylosulphate.*— Greenish blue, silky, very thin laminæ, very soluble in water. (Cahours.) The blue solution of carbonate of copper in the acid yields, when left over oil of vitriol, large elongated tables which are permanent in the air, contain 17·05 p. c. cupric oxide, therefore 4 At. water, dissolve readily in water and weak alcohol, less readily in absolute alcohol, and are insoluble in ether. (Kekulé.)

*Mercuric Amylosulphate.*— The yellow solution of mercuric oxide in the acid yields by evaporation in vacuo, dark yellow, crystalline nodules soapy and glutinous to the touch, having an extremely sharp and bitter taste; they contain 37·8 p. c. mercuric oxide, and therefore 2 At. water; they decompose after keeping for some time and deliquesce in damp air. (Kekulé.)

*Amylosulphate of Silver.*— The solution of carbonate of silver in the slightly heated acid yields by evaporation, colourless laminæ which dissolve very easily in water. (Cahours.) Colourles scales grouped in nodules, which blacken on exposure to the air, and dissolve in alcohol but not in ether. (Kekulé.)

| *Crystals dried in vacuo.* | | | Kekulé. |
|---|---|---|---|
| $C^{10}H^{11}O^2,2SO^3$ | 167 | 60·73 | |
| Ag | 108 | 39·27 | 39·33 |
| $C^{10}H^{11}AgO^2,2SO^3$ | 275 | 100·00 | |

Amylosulphuric acid dissolves readily in *alcohol.* (Cahours.)

## Amyloxanthic Acid.

$$C^{12}H^{12}S^4O^2 = C^{10}H^{12}O^2,2CS^2.$$

Erdmann. (1844). *J. per Chem.* 31, 4.
Balard. *N. Ann. Chim. Phys.* 12, 294; also *J. pr. Chem.* 34, 135.

*Xanthamylic acid, Sulphocarbonate of amyl.*

*Preparation.* A cold-saturated solution of hydrate of potash in fusel-oil is mixed with bisulphide of carbon, till the alkaline reaction disappears, a certain amount of heat being thereby evolved; the crystalline pulp which forms on cooling thrown on a filter; the pale yellow, shining crystalline scales washed with ether, and freed from the yellow mother-liquor by repeated pressure between paper; and the amyloxanthic acid separated from them by hydrochloric acid in the form of an oil, which must be dried over chloride of calcium, to preserve it from decomposition. (Erdmann.)—2. A solution of hydrate of potash in fusel-oil is mixed with a solution of sulphide of carbon in fusel-oil; and the scales which form on cooling separated from the yellow mother-liquor, pressed between paper, and purified by crystallization from hot alcohol or ether. (Balard; *comp.* Koninck, *Berz. Jahresber.* 24, 552.)

*Properties.* Colourless or pale yellow oil, which is somewhat heavier than water, has a disagreeably penetrating odour, colours the skin deep yellow, and reddens litmus. (Erdmann.) Yellow oil. (Balard.)

*Calculation.*

| | | |
|---|---|---|
| 12 C | 72 | 43·90 |
| 12 H | 12 | 7·32 |
| 2 O | 16 | 9·76 |
| 4 S | 64 | 39·02 |
| $C^{12}H^{12}O^2S^4$ | 164 | 100·00 |

The acid burns with a luminous flame and decomposes when kept in the moist state. (Erdmann.)

¶. *Amyloxanthate of Ammonia* $C^{10}H^{11}(NH^4)O^2,2CS^2$.—Produced, together with xanthamylamide, by the action of ammonia on bioxysulphocarbonate of amyl. (*vid. inf.*):

$$2C^{12}H^{11}O^2S^4 + 2NH^3 = C^{12}NH^{13}S^2O^2 + C^{10}H^{11}(NH^4)O^2,2CS^2 + 2S.$$

This salt is contained in the liquid filtered from the xanthamylamide and sulphur, and crystallises from an alcoholic or ethereal solution in long colourless prisms. From a cold aqueous solution evaporated in vacuo, it also separates in prismatic crystals, but is gradually decomposed by water, with formation of an oily liquid. Even the dry crystals decompose on exposure to the air, yielding sulphocyanide of ammonium, and a yellow oil not identical with xanthamylamide. When the aqueous solution of the salt is evaporated over the water-bath, it volatilises together with the watery vapours. It may be sublimed by a very gentle heat; but when more quickly heated in a current of dry air, it decomposes, and at last suddenly, with effervescence, evolution of sulphide of ammonium, and formation of a turbid yellow liquid, from which water dissolves sulphocyanide of ammonium and separates amylic alcohol; caustic potash decomposes the salt, with evolution of ammonia, even in the cold, and quickly when heated.—Hydrochloric acid added to the aqueous solution, separates a volatile oily acid, having a suffocating odour and insoluble in water. (M. W. Johnson, *Chem. Soc. Qu. J.* 5, 147.) ¶.

*Amyloxanthate of Potash* crystallizes in pale yellow, shining, crystalline scales, greasy to the touch. (Erdmann, Balard.) They dissolve in water, forming a yellow very bitter liquid. (Balard.) They dissolve abundantly in hydrated and in absolute alcohol, sparingly in ether. (Erdmann.)

| | | | Balard. |
|---|---|---|---|
| KO | 47·2 | 23·34 | 22·9 |
| 12 C | 72·0 | 35·61 | 35·4 |
| 11 H | 11·0 | 5·44 | 5·3 |
| O | 8·0 | 3·96 | |
| 4 S | 64·0 | 31·65 | |
| $C^{10}H^{11}KO^2,C^2S^4$ | 202·2 | 100·00 | |

*Amyloxanthate of Lead.*—The aqueous solution of the potash salt forms with acetate of lead, a white precipitate which turns black when boiled. (Erdmann.)—¶. The aqueous solution of the ammonia-salt forms with acetate of lead, an adhesive, yellow, semi-solid salt, which gradually

decomposes and turns brown; but on adding the aqueous solution of the ammonia or potash-salt mixed with alcohol, to an alcoholic solution of acetate of lead, till a precipitate begins to appear, and then adding alcohol in excess, a clear solution is obtained, which, by spontaneous evaporation deposits the lead-salt in delicate, shining, plates containing 38·32 p. c. lead, (calculated quantity = 38·85). By decomposing the recently precipitated lead-salt suspended in alcohol, with sulphuretted hydrogen, an acid liquid is obtained, which gives a yellowish white precipitate with alcoholic acetate of lead, and forms a crystalline salt with potash. (Johnson.) ¶.

The aqueous solution of the potash-salt forms with *cupric sulphate*, lemon-yellow flakes; with *mercuric chloride*, a white precipitate which remains white when boiled; and with *nitrate of silver*, a white precipitate which quickly blackens on boiling or on exposure to light. (Erdmann.) The ammonia-salt forms with nitrate of silver a yellow curdy precipitate. (Johnson.)

¶ *Methamylic* and *Vinamylic Oxysulphocarbonates* $\left.\begin{matrix}C^2H^3\\C^{10}H^{11}\end{matrix}\right\}2CS^2O$, and $\left.\begin{matrix}C^4H^5\\C^{10}H^{11}\end{matrix}\right\}2CS^2O$. — Obtained by distilling a mixture of amyloxanthate of potash and sulphomethylate or sulphovinate of potash; *e. g.*

$$\left.\begin{matrix}C^{10}H^{11}\\K\end{matrix}\right\}2CS^2O + \left.\begin{matrix}C^4H^5\\K\end{matrix}\right\}2SO^4 = \left.\begin{matrix}C^4H^5\\C^{10}H^{11}\end{matrix}\right\}2CS^2O + 2KO^4.$$

The methamylic compound heated with dry ammoniacal gas, and digested with it for several months, yielded a substance having all the properties of xanthamylamide:

$$\left.\begin{matrix}C^2H^3\\C^{10}H^{11}\end{matrix}\right\}2CS^2O + NH^3 = \underbrace{C^{12}NH^{13}O^2S^2}_{\text{xanthamylamide.}} + \underbrace{C^2H^4S^2}_{\text{methyl mercaptan.}}$$

[Compare the reaction obtained by Debus with vinomethylic oxysulphocarbonate, (viii, 445)]. The vinamylic oxysulphocarbonate digested with ammonia yielded a yellow mixture which emitted the odour of amylic mercaptan, but did not appear to form xanthamylamide. (Johnson.) [If amyl-mercaptan were formed, the other product must have been xanthamide.]

## Bioxysulphocarbonate of Amyl.

$$C^{12}H^{11}O^2S^4 = C^{10}H^{11}O^2,C^2S^4 = C^{10}H^{11}O,C^2S^4O.$$

DESAINS. *N. Ann. Chim. Phys.* 20, 496; also *J. pr. Chem.* 42, 299.

When hydrate of potash and fusel-oil free from spirit of wine, are rubbed together in a mortar to a thin pulp; sulphide of carbon then added, but not in excess, while the trituration is continued; the resulting amyloxanthate of potash diluted with a small quantity of water; and pulverised iodine triturated at the bottom of the liquid, very slowly, to avoid too great a rise of temperature and consequent separation of sulphur, bioxysulphocarbonate of amyl rises to the surface of the watery liquid containing iodide of potassium, in the form of a yellow oil. (Desains.) — ¶ Johnson (*Chem. Soc. Qu. J.* 5, 142) introduces the amyloxanthate of potash into a flask

together with a quantity of sulphide of carbon sufficient to convert it into a very thin paste, then introduces iodine, which is immediately decolorised, with evolution of heat. On agitation, a grey mixture is formed consisting of roundish granules of iodide of potassium, and a yellow mobile liquid. The whole thrown on a filter and washed with sulphide of carbon, yields a filtrate, which on distilling off the sulphide of carbon, leaves bioxysulphocarbonate of amyl in the form of a yellow oily liquid. ¶.—

| *Dried over chloride of calcium.* | | | Desains. |
|---|---|---|---|
| 12 C | 72 | 44·17 | 43·96 |
| 11 H | 11 | 6·75 | 7·13 |
| 4 S | 64 | 39·26 | |
| 2 O | 16 | 9·82 | |
| $C^{12}H^{11}S^4O^2$ | 163 | 100·00 | |

When bioxysulphocarbonate of amyl obtained as above, is gradually heated in an oil-bath, it boils at 187°; and if the receiver be changed at this point, an amber-coloured oil collects, having a strong ethereal odour and containing 55·0 p. c. C and 9·4 H, therefore $=C^{12}H^{11}OS^2$. (Desains.)

## Nitrite of Amyl.

$C^{10}H^{11}NO^4 = C^{10}H^{11}O,NO^3$.

Balard (1844). *N. Ann. Chim. Phys.* 12, 318
Rieckher. *Jahrb. pr. Pharm.* 14, 1.

*Salpetrigsaures Amyloxyd, Salpetrigmylester, Ether azoti-amylique, Ether azoteux de l'Alcool amylique.*

*Preparation.*. 1. Fusel-oil is gently heated in a retort with nitric acid; the fire quickly removed as soon as bubbles begin to form; the retort cooled if the effervescence is too strong; the portion of the distillate which passes over below 100° (that which goes over between 100° and 148° is contaminated with nitrate of amyl, according to Hofmann), rectified over potash, whereupon ammonia is evolved from the hydrocyanic acid previously formed; and the product which distils over at 96° collected apart. (Balard.) — 2. The nitrous vapours evolved from starch and nitric acid are passed into fusel oil. (Balard.) This liquid is distilled, the nitrous vapours being passed through it all the time; and the distillate is rectified, the portion which distils over at 95° being collected apart. (Rieckher.)

*Properties.* Pale yellow liquid, which assumes a darker yellow colour whenever it is heated, boils at 96°, and yields a reddish yellow vapour of density 4·03. (Balard.) Sp. gr. 0·8773; boiling point 95°. (Rieckher.) Begins to boil at 90°, the boiling point rising slowly to 110°, while red vapours are evolved, then more quickly to 200°, and leaves a small quantity of charcoal. (W. Hofmann, *Ann. Pharm.* 75, 364.) Smells like nitrite of ethyl (Balard), and produces violent head-ache when its vapour is inhaled. (Rieckher.)

| | | | | |
|---|---|---|---|---|
| | | | Balard. | Rieckher. |
| 10 C | 60 | 51·28 | 50·3 | 51·23 |
| 11 H | 11 | 9·40 | 9·5 | 9·75 |
| N | 14 | 11·97 | 13·6 | |
| 4 O | 32 | 27·35 | 26·6 | |
| $C^{10}H^{11}NO^4$ | 117 | 100·00 | 100·0 | |

| | Vol. | Density. |
|---|---|---|
| C-vapour | 10 | 4·1600 |
| H-gas | 11 | 0·7623 |
| N-gas | 1 | 0·9706 |
| O-gas | 2 | 2·2186 |
| Vapour of Nitrite of Amyl | 2 | 8·1115 |
| | 1 | 4·0557 |

*Decompositions.* 1. Nitrite of amyl is decomposed by peroxide of lead with the aid of heat, yielding fusel-oil and nitrate and nitrite of lead;

$$2C^{10}H^{11}NO^4 + 2PbO^2 + 2HO = 2C^{10}H^{12}O^2 + PbO,NO^5 + PbO,NO^3 \text{ (Rieckher).}$$

2. It is but slowly decomposed by aqueous potash (Balard), more quickly by alcoholic potash, with formation of nitrite of potash. (Rieckher.)— 3. When dropped upon melted hydrate of potash, which sometimes sets it on fire, it forms valerate of potash. (Rieckher.)

## Nitrate of Amyl.

$$C^{10}H^{11}NO^6 = C^{10}H^{11}O,NO^5.$$

WILH. HOFMANN (1848). *N. Ann. Chim. Phys.* 23, 374; also *J. pr. Chem.* 45, 358.
RIECKHER. *Jahrb. pr. Pharm.* 14, 1.

*Formation.* When fusel-oil is distilled with nitric acid, nitrite of amyl first passes over, then from 90° upwards, a mixture of nitrite and nitrate. (Hofmann.)

*Preparation.* 10 grammes of nitrate are shaken up in a retort for 10 minutes with 30 grammes of strong nitric acid, 40 grammes of fusel-oil then added, and the mixture gradually heated, a cooled receiver being adapted to the retort. With larger quantities, the action is so violent that scarcely any nitrate of amyl is obtained. The distillate, which collects in two layers, is shaken up with water; the lower layer, after standing for some time, separated by a funnel, then rectified, the receiver being changed after the boiling point has risen from 110° to 148° and become stationary; and the portion which distils over from 148° upwards rectified twice more, the liquid which goes over below 148°, being each time set aside. (Hofmann.) Nitrate of ammonia may be used instead of nitrate of urea. (Rieckher.)

*Properties.* Colourless oil of sp. gr. 0·994 at 10°; boils at 148°. (Hofmann.) Sp. gr. 0·902; boils at 137°. (Rieckher.) Has a peculiar

odour like that of bugs, and has a sweet and burning taste, with very disagreeable aftertaste (Hofmann); its odour is more agreeable than that of any other amylic ether except the acetate. (Rieckher.)

| | | | Hofmann. | Rieckher. |
|---|---|---|---|---|
| 10 C | 60 | 45·11 | 45·65 | 45·13 |
| 11 H | 11 | 8·27 | 8·70 | 8·48 |
| N | 14 | 10·53 | 11·25 | |
| 6 O | 48 | 36·09 | 34·40 | |
| $C^{10}H^{11}NO^6$ | 133 | 100·00 | 100·00 | |

Nitrate of amyl burns with a faint green-edged flame. — Alcoholic potash decomposes it into fusel-oil and nitrate of potash. (Hofmann.)

It dissolves in ether and alcohol, and is precipitated from the latter by water. (Hofmann.)

## Bibasic Silicate of Amyl.

$$C^{20}H^{22}SiO^4 = 2C^{10}H^{11}O,SiO^2.$$

Ebelmen. (1846.) *N. Ann. Chim. Phys.* 16, 155; also *Ann. Pharm.* 57 344; also *J. pr. Chem.* 37, 367.

*Kieselsaures Amyloxyd, Halbkieselmylester, Silicate amylique.*

*Formation.* Chloride of silicium takes up the first quantities of fusel-oil, with depression of temperature and rapid evolution of hydrochloric acid; the following portions, with rise of temperature and slight evolution of hydrochloric acid:

$$2C^{10}H^{12}O^2 + SiCl^2 = C^{20}H^{22}SiO^4 + 2HCl.$$

*Preparation.* On distilling a mixture of the two liquids, hydrochloric acid and the excess of fusel-oil pass over first, then from 320° to 340° (a slight residue then remaining) the silicate of amyl, which may be purified by two rectifications, the first and last portions being each time set aside.

*Properties.* Transparent colourless liquid of sp. gr. 0·868 at 20°; boils at 322° to 325°. Vapour-density 11·70 (the residue in the bulb however appears browned). Has a faint odour like that of fusel-oil.

| | | | Ebelmen. |
|---|---|---|---|
| 20 C | 120 | 63·50 | 63·78 |
| 22 H | 22 | 11·64 | 11·69 |
| 2 O | 16 | 8·46 | 8·52 |
| $SiO^2$ | 31 | 16·40 | 16·01 |
| $C^{20}H^{22}SiO^4$ | 189 | 100·00 | 100,00 |

| | Vol. | Density. |
|---|---|---|
| C-vapour | 20 | 8·3200 |
| H-gas | 22 | 1·6632 |
| Si-vapour ? | 1 | 1·0400 |
| O-gas | 2 | 2·2186 |
| Vapour of $C^{20}H^{22}SiO^4$ | 1 | 13·2418 |

It must be observed that, according to this calculation, the vapour of bibasic silicate of amyl, like that of the corresponding ethyl compound (viii, 479), is not diatomic but monatomic.

*Decompositions.* 1. Bibasic silicate of amyl burns with a long white flame, and deposits silica in the form of a very soft powder. — 2. It is very slowly decomposed by water, in which it does not dissolve. — 3. It is decomposed by alcoholic soda but not by alcoholic ammonia.

*Combinations.* Silicate of amyl mixes in all proportions with alcohol, ether, and fusel-oil. (Ebelmen.)

## Formiate of Amyl.

$$C^{12}H^{12}O^4 = C^{10}H^{11}O,C^2HO^3.$$

HERMANN KOPP. (1845.) *Ann. Pharm.* 55, 183.

*Preparation.* 6 pts. of dry formiate of soda are distilled with 7 pts. of fusel-oil and 6 pts. of oil of vitriol; the layer of liquid below the formiate of amyl which has passed over, diluted with water, whereby an additional quantity of the compound ether is separated; and the decanted ether washed with aqueous carbonate of soda, then with water, digested over chloride of calcium, and twice rectified, only the more volatile portion being collected.

*Properties.* Transparent, colourless, thin liquid, of sp. gr. 0·8743 at 21°, boiling at 16° under a pressure of 27″8‴, and having an agreeable fruity odour.

| | | | Kopp. |
|---|---|---|---|
| 12 C | 72 | 62·07 | 61·6 |
| 12 H | 12 | 10·35 | 10·5 |
| 4 O | 32 | 27·58 | 27·9 |
| $C^{12}H^{12}O^4$ | 116 | 100·00 | 100·0 |

The ether quickly turns acid in vessels containing air. It dissolves sparingly in water. (Kopp.)

## Chloroformiate of Amyl.

$$C^{12}H^{11}ClO^4 = C^{10}H^{11}O,C^2ClO^3.$$

CAHOURS. (1847.) *N. Ann. Chim. Phys.* 19, 351.
MEDLOCK. *Ann. Pharm.* 69, 217 and 71, 104; also *Chem. Soc. Qu. J.* 1, 368 and 2, 252.

*Chlorocarbonate of Amyl, Chlorkohlensaures Amyloxyd, Chlorameisenmylester.*

*Formation and Preparation.* 1. Perchloroxalate of methyl is resolved by fusel-oil into hydrochloric acid, oxalate of amyl, and chloroformiate of amyl. (Cahours, ix, 177.) — 2. Pure fusel-oil introduced into a flask filled with phosgene gas, absorbs it rapidly, with great evolution of heat, 1 gramme of fusel-oil taking up about a litre of gas. (Medlock.)

$$C^{10}H^{12}O^2 + 2CClO = C^{12}H^{11}ClO^4 + HCl.$$

*Properties.*— Very pungent-smelling liquid, boiling between 150° and 160°. (Cahours.) Amber-coloured oil. (Medlock.)

*Decompositions.* 1. Chloroformiate of amyl begins to boil at 180° when distilled from a perfectly dry retort; but the boiling point quickly rises to 224°, and thence, but slowly, higher, the ether being at the same time converted, with evolution of hydrochloric acid, into carbonate of amyl (no more forming a solid compound with ammonia), of which both the distillate and the residue are then found to consist. (Medlock.) In presence of water, the equation is

$$C^{12}H^{11}ClO^4 + HO = C^{11}H^{11}O^3 + CO^2 + HCl;$$

in the absence of water, the carbonate of amyl is formed from a portion of the chloroformiate itself; so that in this case a large quantity of charred matter remains in the retort. (Medlock.)—2. It mixes with aqueous ammonia, producing intumescence, and the oil which rises to the surface solidifies on cooling, in a crystalline mass consisting of carbonate of amyl and sal-ammoniac. (Medlock.)

$$C^{12}H^{11}ClO^4 + 2NH^3 = C^{12}NH^{13}O^4 + NH^4Cl \text{ (Medlock).}$$

## Valerate of Methyl.

$$C^{12}H^{12}O^4 = C^2H^3O,C^{10}H^9O^3.$$

H. Kopp. (1845.) *Ann. Pharm.* 55, 185.—*Pogg.* 72, 287.

*Preparation.* 4 pts. of valerate of soda are distilled with 4 pts. of wood-spirit and 3 pts. of oil of vitriol, with one cohobation; the distillate shaken up with milk of lime; repeatedly dehydrated over chloride of calcium; rectified after decantation therefrom; and again rectified with a fresh receiver, the portion which distils over between 114° and 115°, with a platinum wire immersed in the liquid, being collected apart.

*Properties.* Transparent, colourless liquid of sp. gr. 0·8869 at 15°; boiling at 116·2° with platinum wire immersed, and having a strong aromatic odour like wood-spirit and valerian. (Kopp.)

| | | | Kopp. |
|---|---|---|---|
| 12 C | 72 | 62·07 | 61·20 |
| 12 H | 12 | 10·34 | 10·33 |
| 4 O | 32 | 27·59 | 28·47 |
| $C^{12}H^{12}O^4$ | 116 | 100·00 | 100·00 |

## Cyanide of Amyl.

$$C^{12}NH^{11} = C^{10}H^{10},C^2NH. \ ?$$

Balard. (1844.) *N. Ann. Chim. Phys.* 12, 294; also *J. pr. Chem.* 34, 136.
Frankland & Kolbe. *Ann. Pharm.* 65, 297.
Brazier & Gossleth. *Ann. Pharm.* 75, 251.

*Cyanamyl, Cyanmylafer, Ether cyanhydramylique.*

Formed: 1. By heating cyanide of potassium with amylosulphate of potassium:

$$C^2NK + C^{10}H^{11}KO^2,2SO^3 = C^{12}NH^{11} + 2(KO,SO^3).$$

2. By heating cyanide of potassium with chloride of amyl, chloride of potassium being separated at the same time:

$$C^2NK + C^{10}H^{11}Cl = C^{12}NH^{11} + KCl.$$

3. By heating cyanide of potassium with oxalate of amyl:

$$2C^2NK + C^{24}H^{22}O^8 = 2C^{12}NH^{11} + C^4K^2O^8 \text{ (Balard).}$$

An intimate mixture of cyanide of potassium and amylosulphate of potassium in equal numbers of atoms is distilled, and the distillate shaken up several times with water, then dried over chloride of calcium, and rectified. (Frankland and Kolbe.)

Thin liquid of sp. gr. 0·806 at 20°; boiling steadily at 146°; having a vapour density of 3·335, and a peculiar, not very unpleasant odour. (Frankland & Kolbe.)

| | | | Frankland & Kolbe. |
|---|---|---|---|
| 12 C | 72 | 74·23 | 74·37 |
| N | 14 | 14·43 | |
| 11 H | 11 | 11·34 | 11·67 |
| $C^{12}NH^{11}$ | 97 | 100·00 | |

| | Vol. | Density. |
|---|---|---|
| C-vapour | 12 | 4·9920 |
| N-gas | 1 | 0·9706 |
| H-gas | 11 | 0·7623 |
| Vap. of $C^{12}NH^{11}$ | 2 | 6·7249 |
| | 1 | 3·3624 |

Cyanide of amyl is decomposed by boiling with aqueous, and more quickly with alcoholic potash, yielding ammonia and caproate of potash:

$$C^{12}NH^{11} + 3HO + KO = C^{12}H^{11}KO^4 + NH^3.$$

With potassium, it yields, together with gaseous products, an alkaloid corresponding to cyanethine. (Medlock, *Ann. Pharm.* 69, 229.)

It dissolves sparingly in water, and in all proportions in *alcohol*. (Frankland & Kolbe.)

## Sulphocyanide of Amyl.

$$C^{12}NH^{11}S^2 = C^{10}H^{10},C^2NHS^2 ?$$

O. Henry. (1849.) *N. Ann. Chim. Phys.* 25, 246; also *N. J. Pharm.* 14, 248; also *J. pr. Chem.* 46, 161.

Medlock. *Chem. Soc. Qu. J.* 1, 373; *Ann. Pharm.* 69, 222.

*Schwefelcyanamyl, Schwefelcyan-mylafer, Sulfocyanure d'Amyle.*

*Formation and Preparation.* 1. Crystallized amylosulphate and crystallised sulphocyanide of potassium in about equal volumes, are distilled together in a large retort with a cooled receiver; the yellow oil which passes over separated from the water, dried over chloride of

calcium, and rectified; and this treatment with chloride of calcium and rectification repeated several times (Henry):

$$C^{10}H^{11}KO^2,2SO^3 + C^2NKS^2 = C^{12}NH^{11}S^2 + 2(KO,SO^3).$$

2. When an intimate mixture of 2 pts. amylosulphate of lime and 1 pt. of sulphocyanide of potassium — which, to avoid violent intumescence, must be dried as completely as possible — is distilled in a retort of twice the capacity of the mixture, there is obtained, after a small quantity of water having a very peculiar odour has passed over, a yellow oil having the same odour. This oil is distilled with water; removed with the pipette; dried over chloride of calcium, which withdraws the last quantities of water with difficulty, and dissolves somewhat abundantly; and rectified, the boiling point rising from 150° to 195°, from which point upwards the greater part is to be distilled into a fresh receiver. This last portion, again subjected to fractional rectification, yields the pure sulphocyanide of amyl, boiling at 197°. (Medlock.)

*Properties.* Thin colourless liquid. (Henry.) Pale yellow oil, boiling steadily at 197°. (Medlock.) It begins to boil at 170°, the greater portion passing over between 195° and 210°, but the remainder not till the temperature rises to 260°; the oil which passes over after repeated rectification between 210° and 240° has a density of 0·905 at 20°. (Henry.) Has a pungent alliaceous odour. (Henry.)

| | | | Henry. | Medlock. |
|---|---|---|---|---|
| 12 C | 72 | 55·81 | 56·86 | 55·69 |
| N | 14 | 10·85 | | 10·84 |
| 11 H | 11 | 8·52 | 8·81 | 8·95 |
| 2 S | 32 | 24·82 | | |
| $C^{12}NH^{11}S^2$ | 129 | 100·00 | | |

The ether analysed by Henry was collected between 195° and 210°.

*Decomposition.* Moderately strong nitric acid acts violently on the compound, giving off nitrous vapours, nitrogen gas and carbonic acid, and forming amylosulphurous acid together with a small quantity of sulphuric acid. (Henry; Medlock.)

## Acetate of Amyl.

$$C^{14}H^{14}O^4 = C^{10}H^{11}O,C^4H^3O^3.$$

Cahours. (1840.) *Ann. Chim. Phys.* 75, 193; also *Ann. Pharm.* 37, 167; also *J. pr. Chem.* 22, 171.
Hermann Kopp. *Ann. Pharm.* 55, 187.

*Amylic Acetate, Essigsaures Amyloxyd, Essig-mylester, Acetate d'Amylène.*— The so-called *pear oil* used in perfumery consists of this ether. (A. W. Hofmann, *Ann. Pharm.* 81, 87.)

*Formation.* This compound is produced even by leaving a mixture of fusel-oil and moderately strong acetic acid to stand for several days. (Dobereiner.)

*Preparation.* 2 pts. of acetate of potash are distilled with 1 pt. of fusel-oil and 1 pt. oil of vitriol; the distillate washed with water containing potash, dried over chloride of calcium, and rectified over oxide of lead. (Cahours.)—2. The distillate obtained from 3 pts. of dehydrated acetate of lead, 1 pt. of fusel-oil and 1 part oil of vitriol, is shaken up with milk of lime, dehydrated over chloride of calcium and rectified, the small portion which passes over below 133° and becomes turbid when mixed with water, and that also which distils above 140°, being set aside. In the retort there remains a turbid liquid, amounting to $\frac{1}{5}$ of the whole, which deposits crystalline spangles and becomes clear. (Kopp.)

*Properties.* Transparent, colourless liquid, lighter than water (Cahours), of sp. gr. 0·8572 at 21°. (Kopp.) Boils at 125° (Cahours); with a platinum-wire immersed in it, it boils constantly at 133·3° under a pressure of 27″ 8‴. (Kopp.) Vapour density = 4·458. Odour, ethereal and aromatic, somewhat like that of acetate of ethyl. (Cahours.)

| | | | Cahours. | Kopp. |
|---|---|---|---|---|
| 14 C | 84 | 64·61 | 64·47 | 64·08 |
| 14 H | 14 | 10·77 | 10·68 | 10·98 |
| 4 O | 32 | 24·62 | 24·85 | 24·94 |
| $C^{14}H^{14}O^4$ | 130 | 100·00 | 100·00 | 100·00 |

| | Vol. | Density. |
|---|---|---|
| C-vapour | 14 | 5·8240 |
| H-gas | 14 | 0·9702 |
| O-gas | 2 | 2·2186 |
| Vapour of Amylic Acetate | 2 | 9·0128 |
| | 1 | 4·5064 |

*Decompositions.* 1. Well dried acetate of amyl absorbs chlorine gas passed through it, becoming heated thereby, and, when treated with chlorine at 100°, as long as hydrochloric acid continues to escape, is converted into chloracetate of amyl, $C^{14}C^2H^{12}O^4$, which, by the action of chlorine in sunshine, is converted into a higher chlorine-compound.—2. It is not coloured by oil of vitriol in the cold, but when heated therewith, it becomes reddish yellow, then black, and gives off sulphurous acid.—3. It is decomposed very slowly by aqueous, but quickly by alcoholic potash, into acetate of potash and fusel-oil. (Cahours.)

*Combinations.* Insoluble in water, but dissolves in *alcohol, ether,* and *fusel-oil.* (Cahours.)

## Chloracetate of Amyl.

$$C^{14}Cl^2H^{12}O^4 = C^{10}H^{11}O,C^4Cl^2HO^3.$$

Cahours. (1840.) *Ann. Chim. Phys.* 79, 193.

*Chlorhaltiges essigsaures Amyloxyd, Chloressigmylester, Acetate d'Amylène chloré.*

*Preparation.* Dry chlorine gas is passed through well dried acetate of amyl, first at the ordinary temperature, then at 100°, as long as

hydrochloric acid gas continues to be evolved; and the product washed with aqueous carbonate of soda, then with a large quantity of pure water, and dried in vacuo over oil of vitriol.

*Properties.* Thin colourless oil, heavier than water and having an agreeable odour.

| | | | Cahours. |
|---|---|---|---|
| 14 C | 84·0 | 42·26 | 42·26 |
| 2 Cl | 70·8 | 35·61 | 35·29 |
| 12 H | 12·0 | 6·03 | 6·07 |
| 4 O | 32·0 | 16·10 | 16·38 |
| $C^{14}Cl^2H^{12}O^4$ | 198·8 | 100·00 | 100·00 |

*Decompositions.* 1. Chloracetate of amyl assumes a strong yellow colour at 150°, and decomposes completely when distilled.—2. When exposed for some time to the sun in a bottle filled with chlorine-gas, it does not thicken, but deposits small needles, and in the end is probably converted wholly into $C^{14}Cl^{14}O^4$. (Cahours.)

It is insoluble in water, but dissolves in alcohol and still more readily in ether. (Cahours.)

## Valerate of Ethyl.

$$C^{14}H^{14}O^4 = C^4H^5O,C^{10}H^9O^3.$$

OTTO. (1838.) *Ann. Pharm.* 25, 62; 27, 225.
H. KOPP. *Ann. Pharm.* 55, 187.

*Valerianic ether, Baldrian-vinester.*

*Preparation.* 8 pts. of valerate of soda are distilled with 10 pts. of 88 per cent. alcohol and 5 pts. oil of vitriol; the resulting valerate of ethyl, a portion of which separates from the distillate only on addition of water, washed with dilute carbonate of soda, then with pure water, dehydrated over chloride of calcium, decanted, and distilled with a platinum-wire immersed in it; and the portion which distils at 133° collected apart. (Kopp.)

*Properties.* Transparent, colourless liquid, of sp. gr. 0·894 at 13° (Otto); 0·8659 at 18° (Kopp); 0·869 at 14° (Berthelot, *N. Ann. Chim. Phys.* 41, 254); 0·870 at 13·5°. (Delffs.) Boils at 133·5° (Otto); at 133·2°, with platinum-wire immersed (Kopp); at 131·5°, with the bar. at 325·7° mm. (Delffs); between 133° and 134°. (Berthelot.) Vapour-density 4·558. Odour penetrating, like fruit and valerian. (Otto.) Index of refraction for the red ray, 1·3904. (Delffs, *N. Jahrb. Pharm.* 1, 1.)

| | | | Otto. | Kopp. | Berthelot. |
|---|---|---|---|---|---|
| 14 C | 84 | 64·61 | 64·84 | 64·00 | 64·2 |
| 14 H | 14 | 10·77 | 10·79 | 10·97 | 11·0 |
| 4 O | 32 | 24·62 | 24·37 | 25·03 | 24·8 |
| $C^{14}H^{14}O^4$ | 130 | 100·00 | 100·00 | 100·00 | 100·0 |

| | Vol. | | Density. |
|---|---|---|---|
| C-vapour | 14 | .... | 5·8240 |
| H-gas | 14 | .... | 0·9702 |
| O-gas | 2 | .... | 2·2186 |
| Vapour of Valerianic ether .... | 2 | .... | 9·0128 |
| | 1 | .... | 4·5064 |

Berthelot's product was prepared with valerianic acid obtained from dolphin-oil.

*Decompositions.* Strong ammonia decomposes valerate of ethyl in a few weeks, into valeramide and alcohol. (Dumas, Malaguti & Leblanc; Dessaignes & Chautard):

$$C^{14}H^{14}O^4 + NH^3 = C^{10}NH^{11}O^2 + C^4H^6O^2.$$

## Oxalate of Amyl.

$$C^{24}H^{22}O^8 = 2C^{10}H^{11}O,C^4O^6.$$

BALARD. (1844.) *N. Ann. Chim. Phys.* 12, 309; also *J. pr. Chem.* 34, 137.
CAHOURS. *N. Ann. Chim. Phys.* 19, 351.

*Oxalsaures Amyloxyd, Oxal-mylester, Ether oxalamylique.*

*Preparation.* 1. When fusel-oil is heated with a large excess of crystallised oxalic acid, two layers are formed, the lower consisting of aqueous oxalic acid, and the upper of an oil which smells like bugs, and deposits oxalic acid on cooling. On distilling this oil, collecting apart the portion which goes over at 262°, and rectifying this portion with the same precaution, the pure oxalate of amyl is obtained. (Balard.) — 2. When perchloroxalate of methyl (ix, 176), is decomposed by fusel-oil, oxalate of amyl is obtained together with the perchloro-formiate (p. ) (Cahours.)

*Properties.* Colourless liquid boiling at 262° (260° according to Cahours), having a vapour-density of 8·4, and a strong odour of bugs. (Balard.)

| | | | | | | Balard. | | Cahours. |
|---|---|---|---|---|---|---|---|---|
| 24 C | 144 | .... | 62·61 | .... | | 62·4 | .... | 62·30 |
| 22 H | 22 | .... | 9·56 | .... | | 9·7 | .... | 9·56 |
| 8 O | 64 | .... | 27·83 | .... | | 27·9 | .... | 28·14 |
| $C^{24}H^{22}O^8$ | 230 | .... | 100·00 | .... | | 100·0 | .... | 100·00 |

*Decompositions.* 1. Oxalate of amyl is decomposed by water and more quickly by aqueous fixed alkalis, into fusel-oil and oxalic acid.— 2. With dry ammoniacal gas, it yields oxamylene and fusel-oil:

$$C^{24}H^{22}O^8 + NH^3 = C^{14}NH^{13}O^6 + C^{10}H^{12}O^2.$$

3. With aqueous ammonia it is converted into oxamide and fusel-oil;

$$C^{24}H^{22}O^8 + 2NH^3 = C^4N^2H^4O^4 + 2C^{10}H^{12}O^2,$$

4. With cyanide of potassium, it yields oxalate of potash and cyanide of amyl:

$$C^{24}H^{22}O^{8} + 2C^{2}NK = C^{4}K^{2}O^{8} + 2C^{12}NH^{11} \text{ (Balard).}$$

## Amyloxalic Acid.

$$C^{14}H^{12}O^{8} = C^{10}H^{12}O^{2},C^{4}O^{6}.$$

Balard. (1844.) *N. Ann. Chim. Phys.* 12, 309; also *J. pr. Chem.* 34, 137.

*Oxamylic acid, Oxalamylic acid.*

When the oil obtained by heating fusel-oil with excess of crystallised oxalic acid (*vid. sup.*), is saturated with carbonate of lime after being separated from the watery layer, the liquid yields by evaporation, crystallised amyloxalate of lime, from which the other salts may be prepared.

*Amyloxalate of Potash.*—Obtained by precipitating the lime-salt with carbonate of potash, and evaporating the filtrate. Needles unctuous to the touch and having a pearly lustre.

*Amyloxalate of Lime.*—Rectangular laminæ, which, when heated to 100° in a current of air, or after solution in water, are resolved into fusel-oil, oxalate of lime and free oxalic acid; they dissolve more readily in hot than in cold water.

| *Crystals.* | | | Balard. |
|---|---|---|---|
| CaO | 28 | 14·21 | 13·9 |
| 14 C | 84 | 42·63 | 41·8 |
| 11 H | 11 | 5·59 | 5.4 |
| 7 O | 56 | 28·43 | |
| 2 HO | 18 | 9·14 | |
| $C^{14}H^{11}CaO^{8} + 2Aq$ | 197 | 100·00 | |

*Amyloxalate of Silver.*—By mixing the lime-salt with a solution of silver, the silver-salt is obtained in anhydrous laminæ, which are unctuous to the touch, have a pearly lustre, dissolve sparingly in water, and decompose by keeping into oxalate of silver, free oxalic acid, and a substance which cannot be fusel-oil, as there is not enough water to produce it. (Balard.)

| *Crystals.* | | | Balard. |
|---|---|---|---|
| 14 C | 84 | 31·46 | 30·2 |
| 11 H | 11 | 4·12 | 3·9 |
| Ag | 108 | 40·45 | 39·6 |
| 8 O | 64 | 23·97 | 26·3 |
| $C^{14}H^{11}AgO^{8}$ | 267 | 100·00 | 100·0 |

## Allophanate of Amyl. ?

$$C^{14}N^2H^{14}O^6 = C^{10}H^{11}O,C^4N^2H^3O^5. \ ?$$

LIEBIG. (1846.) *Ann. Pharm.* 57, 128.
SCHLIEPER. *Ann. Pharm.* 59, 23.
RIECKHER. *Jahrb. pr. Pharm.* 14, 1.
WURTZ. *Compt. rend.* 29, 186.

*Cyanurate of Amyl, Cyansaures Amyloxyd, Allophan-mylester.*

*Formation and Preparation.* 1. When the vapour of cyanic acid evolved from heated cyanuric acid is passed into anhydrous fusel-oil, crystals of this compound ether are obtained and may be purified by crystallisation from water. (Liebig.) Fusel-oil absorbs the vapour of cyanic acid, with great evolution of heat, becomes viscid, and deposits laminæ, in consequence of which it solidifies to a stiff magma on cooling. This mass is boiled with water, which is renewed from time to time, till the odour of fusel-oil is no longer perceptible, then filtered from the cyamelide (ix, 462), into which part of the cyanic acid has been converted, and left to crystallise by cooling. (Schlieper.) — 2. Cyanate of potash is distilled with amylosulphate of potash. (Wurtz.) [Is not the addition of sulphuric acid necessary ?]

*Properties.* Snow-white, nacreous, bulky scales, unctuous to the touch (Schlieper); deceptively like leucin. (Liebig.) Melts when gently heated, and sublimes between two watch-glasses, even at 100°, in shining laminæ. Destitute of taste and smell; neutral to vegetable colours. (Schlieper.)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | | | | | Schlieper. | | Rieckher. |
| 14 C | 84 | .... | 48·28 | .... | 48·62 | | |
| 2 N | 28 | .... | 16·09 | .... | 16·36 | .... | 18·08 |
| 14 H | 14 | .... | 8·05 | .... | 8·08 | | |
| 6 O | 48 | .... | 27·58 | .... | 26·94 | | |
| $C^{14}N^2H^{14}O^6$ | 174 | .... | 100·00 | .... | 100·00 | | |

Schlieper regards the body as a compound of 3 At. amylic ether with 2 At. cyanuric acid = $3C^{10}H^{11}O + 2C^6N^3H^3O^6$; but its analogy with allophanate of ethyl (ix, 268) is quite unmistakable.

*Decompositions.* 1. The ether when heated above its melting point, boils, gives off a large quantity of amylic alcohol, and leaves a crystalline residue of pure cyanuric acid:

$$3C^{14}N^2H^{14}O^6 = 3C^{10}H^{12}O^2 + 2C^6N^3H^3O^6.$$

2. When distilled with aqueous alkalis, it readily gives off fusel-oil. (Schlieper.) By hot potash-solution it is converted into carbonate of potash, amylamine [and ammonia]. (Wurtz):

$$C^{14}N^2H^{14}O^6 + 4KO + 2HO = 4(KO,CO^2) + C^{10}NH^{13} + NH^3.$$

It is not decomposed by chlorine, bromine, nitric acid, sulphuretted hydrogen, or ammonia. (Schlieper.)

*Combinations.* The ether is not wetted or dissolved by cold water, but dissolves readily in hot water; the saturated solution becomes covered with an irridescent film, and on cooling deposits the ether in large flakes and needles, which assume the scaly aspect when dry. (Schlieper.)

The aqueous solution does not precipitate any metallic salt. (Schlieper.)

Allophanate of amyl dissolves with tolerable facility in vinic ether (whereby it is distinguished from leucin) (Liebig); also in alcohol, whence it is precipitated by water. (Schlieper.)

## ¶. Monovalerin.

$$C^{16}H^{16}O^{8} = C^{6}H^{8}O^{6},C^{10}H^{8}O^{2} = C^{6}\left\{\begin{matrix} H^{7} \\ C^{10}H^{9}O^{2} \end{matrix}\right\}O^{6}.$$

BERTHELOT. *N. Ann. Chim. Phys.* 41, 254.

*Monophocenin.*

Formed by the action of valerianic acid upon glycerine in excess at a high temperature:

$$C^{10}H^{10}O^{4} + C^{6}H^{8}O^{6} = C^{16}H^{16}O^{8} + 2HO.$$

A mixture of the strongest valerianic acid and excess of glycerine is heated to 200° in a sealed tube for three hours; the mixture when cold, supersaturated with carbonate of potash; a small quantity of caustic potash then added; the liquid shaken up with animal charcoal; the filtrate evaporated over the water-bath; and the residue dried in vacuo on a strongly heated sand-bath.

Oily, neutral, odorous liquid, of sp. gr. 1·100 at 16°.

| | | | Berthelot. | | |
|---|---|---|---|---|---|
| 16 C | 96 | 54·5 | 52·2 | 53·3 | 52·6 |
| 16 H | 16 | 9·1 | 9·1 | 9·2 | 8·6 |
| 8 O | 64 | 36·4 | 38·7 | 37·5 | 38·8 |
| $C^{16}H^{16}O^{8}$ | 176 | 100·0 | 100·0 | 100·0 | 100·0 |

Metameric with butyric acid.

Decomposed in a few hours at ordinary temperatures by hydrochloric acid and alcohol, yielding glycerine and valerate of ethyl.

1 vol. monovalerin treated with $\frac{1}{2}$ vol. water forms a limpid mixture, another $\frac{1}{2}$ vol. water causes the valerin to separate out in a mass; 8 or 10 vol. water produce the same precipitation. With 100 times its volume of water, monovalerin forms a solution or rather an emulsion.

A valerin is also obtained by heating a mixture of glycerine and valerianic acid to 100° in an atmosphere of hydrochloric acid gas. The product contains chlorhydrin. (Berthelot.)

## ¶. Bivalerin.

$$C^{26}H^{24}O^{10} = C^6H^8O^6,(C^{10}H^8O^2)^2 = C^6\left\{\begin{matrix} H^6 \\ (C^{10}H^9O^2)^2 \end{matrix}\right\}O^6.$$

BERTHELOT. *N. Ann. Chim. Phys.* 41, 255.

*Divalerin, Diphocenin.*

Prepared by heating to 275° a mixture of glycerine and valerianic acid slightly diluted with water, and treating the product as in the preparation of monovalerin.

$$[2C^{10}H^{10}O^4 + C^6H^8O^6 = C^{26}H^{24}O^{10} + 4HO].$$

Oily neutral liquid, of sp. gr. 1·059 at 16°. Has a disagreeable odour like that of fish-oil, and a bitter aromatic taste. Solidifies at −40°, becoming semi-soft but retaining its transparency.

| | | | Berthelot. | |
|---|---|---|---|---|
| 26 C | 156 | 60·0 | 55·6 | 55·2 |
| 24 H | 24 | 9·2 | 9·9 | 9·5 |
| 10 O | 80 | 30·8 | 34·5 | 35·3 |
| $C^{26}H^{24}O^{10}$ | 260 | 100·0 | 100·0 | 100·0 |

[Berthelot gives the formula $C^{26}H^{26}O^{12}$, which certainly agrees much better with his analysis, requiring 56·1 C and 9·4 H. The formula above given is however much more probable (see ix, 491); most probably the substance analysed by Berthelot was impure.]

Bivalerin is decomposed by baryta, yielding valerate of baryta. — Treated with hydrochloric acid and alcohol at ordinary temperatures, it is decomposed, yielding glycerine and valerate of ethyl. — The same products of decomposition are obtained by heating a solution of bivalerin in alcohol to 100° for 63 hours. The formation of valerianic ether takes place even on exposing the alcoholic solution to the air at ordinary temperatures; in a closed vessel, only traces of decomposition are observed. — Water, acetic acid and aqueous hydrochloric acid, heated to 100° with bivalerin for 63 hours, decompose it with reproduction of valerianic acid; with water, this effect takes place in a slight degree only; but with hydrochloric acid, it is considerable. — Ammonia slowly changes bivalerin into crystallised valeramide.

1 vol. bivalerin and $\frac{1}{2}$ vol. water do not form a limpid mixture; 8 to 10 vol. water form a very instable emulsion from which the bivalerin separates in a mass, which is not dissolved, even by the gradual addition of a large quantity of water. (Berthelot.)

## ¶ Trivalerin.

$$C^{36}H^{32}O^{12} = C^6H^8O^6,(C^{10}H^8O^2)^3 = C^6\left\{\begin{matrix} H^5 \\ (C^{10}H^9O^2)^3 \end{matrix}\right\}O^6.$$

BERTHELOT. *N. Ann. Chim. Phys.* 41, 257.

*Triphocenin.*

Obtained by heating to 220° for eight hours, a mixture of bivalerin with 8 to 10 times its weight of valerianic acid:

$$3C^{10}H^{10}O^{4} + C^{6}H^{8}O^{6} = C^{36}H^{32}O^{12} + 6HO.$$

Oily, neutral liquid having a faint disagreeable odour. Treated at ordinary temperatures with hydrochloric acid and alcohol, it is resolved in two days into glycerine and valerate of ethyl. — It is insoluble in water, but soluble in alcohol and in ether.

| | | | Berthelot. |
|---|---|---|---|
| 36 C | 216 | 62·8 | 61·6 |
| 32 H | 32 | 9·3 | 9·0 |
| 12 O | 96 | 27·9 | 29·4 |
| $C^{36}H^{32}O^{12}$ | 344 | 100·0 | 100·0 |

The valerins, when exposed to the air, become completely acidified in the course of a few weeks, acquiring the odour of valerianic acid. The elimination of this acid is not due to oxidation; for bivalerin and monovalerin placed in an atmosphere of moist oxygen for 2½ months, absorb but very small quantities of it; it is only when the liquid is in contact with brass filings, that the absorption becomes perceptible. It then amounts to about 2 per cent. of the weight of the oil. (Berthelot.) ¶.

## Delphinin or Phocenin.

$$C^{46}H^{40}O^{14}\ ? = C^{6}H^{4}O^{2},4C^{10}H^{9}O^{3}.\ ?$$

Chevreul. (1818.) *Ann. Chim. Phys.* 22, 374. — *Recherches sur les corps gras.* 190, 287 and 467.

*Baldrianfett, Delphinfett, Phocénine.* — Found in the oil of *Delphinus globiceps, D. phocæa* and *D. marginatus;* not yet obtained in the pure state, the olein not having been completely separated.

*Preparation.* 100 pts. of dolphin-oil are dissolved in 90 pts. of warm alcohol of sp. gr. 0·797; the solution decanted from the oil which is precipitated on cooling, and distilled with water; the oil which remains in the retort, and consists of a mixture of delphinin and olein, separated from the watery liquid, and treated with cold dilute alcohol; and the alcohol evaporated, after the solution has been separated from the undissolved olein.

*Properties.* Oil very mobile at 17°; of sp. gr. 0·954 [0·948 (Berthelot)]; having a faint, peculiar, somewhat ethereal odour like that of valerianic acid; not reddening litmus. [Boiling point 258° (Berthelot).]

*Decompositions.* 1. The alcoholic solution diluted with a large quantity of water, and distilled, leaves delphinin which reddens litmus, from containing free valerianic acid. The fat, when exposed to warm air, likewise acquires the power of reddening litmus, and a strong odour proceeding from the liberated valerianic acid. — 2. Delphinin heated to 100° with an equal quantity of oil of vitriol, and then left to itself, gives off, after a week, the odour of valerianic and sulphurous acid;

water added to it takes up sulphuric, sulphoglyceric, and valerianic acid, and glycerine, and leaves an oily mixture of valerianic acid, oleic acid, and a small quantity of unsaponified fat. — 3. A hundred parts of delphinin saponified with potash, yield 36 pts. valerianic acid, 59 pts. oleic acid, and 15 pts. of glycerine.

¶. 100 pts. of the oil of the common porpoise (*Delphinus phocæa*) saponified with baryta, yielded 82·2 pts. of fixed fatty acids, 16·0 pts. phocenate (valerate) of baryta, and 14·0 glycerine, or 6·7 pts. glycerine to 10·0 pts. valerianic acid ($C^{10}H^{10}O^4$). The same oil treated with alcohol yielded successively three oils, containing respectively 4·4 pts., 4·4 pts. and 5·1 pts. glycerine to 10 pts. valerianic acid. The first of these three oils when again treated with alcohol, yielded a new liquid (phocenin) containing 2·7 pts. glycerine to 10 pts. of valerianic acid. (Chevreul.) The oil of *Delphinus globiceps* was found to contain, besides fixed fatty acids and ethal, 5·9 pts. glycerine to 10·0 valerianic acid. Now for 10 pts. of valerianic acid, monovalerin contains 9·0 pts., bivalerin 4·5 pts., and trivalerin 3·0 pts. of glycerine. Hence it appears that phocenin is intermediate in composition between the artificial valerins, and may therefore be regarded as a mixture of them—a conclusion further warranted by its separation into valeric acid and glycerine by saponification. (Berthelot.) ¶.

*Combinations.* Dissolves abundantly in hot alcohol. (Chevreul.)

## Valerone.

$$C^{18}H^{18}O^2 = C^{10}H^{10}O^2,C^8H^8.$$

Löwig. (1837.) *Pogg.* 42, 212.

*Preparation.* Valerianic acid is cautiously heated in a distillatory apparatus with excess of lime, and the distillate purified by rectification over fresh lime.

*Properties.* Colourless, very thin liquid, lighter than water, boiling much below 100°, having an agreeably ethereal odour like valerianic acid, a cooling ethereal taste, and perfectly neutral.

| | | | Löwig. |
|---|---|---|---|
| 18 C | 108 | 76·06 | 75·36 |
| 18 H | 18 | 12·67 | 12·40 |
| 2 O | 16 | 11·27 | 12·24 |
| $C^{18}H^{18}O^2$ | 142 | 100·00 | 100·00 |

*Decompositions.* 1. Valerone burns with a very smoky flame. — 2. It becomes less heated than acetone by contact with potassium, and the mass formed therewith separates, on addition of water, an oil which exhibits similar properties to that obtained with acetone (ix, 15, 16). (Löwig.)

Chancel (*Compt. rend.* 21, 905) regards Löwig's valerone as a mixture of a very small quantity of valerone with a very large quantity of valeral.

## ¶ Valeracetone.

$$C^{12}H^{12}O^2 = C^{10}H^{10}O^2,C^2H^2 = C^4H^4O^2,C^8H^8.$$

WILLIAMSON. *Chem. Soc. Qu. J.* 4, 238.

Formed by distilling a mixture of acetate of soda [or potash] and valerate of potash in equal numbers of atoms:

$$C^4H^3KO^4 + C^{10}H^9KO^4 = C^{12}H^{12}O^2 + 2(KO,CO^2).$$

The salts were dissolved in water, and evaporated to dryness, the mixture distilled in a retort; the oily distillate shaken up with aqueous potash to remove undecomposed acids, and after separation from the potash. distilled with the thermometer. By uniting the products of several distillations, a liquid was obtained, boiling with perfect regularity at 120°, and constituting nearly two-thirds of the entire distillate:

| | | | Williamson. |
|---|---|---|---|
| 12 C | 72 | 72 | 71·38 |
| 12 H | 12 | 12 | 12·12 |
| 2 O | 16 | 16 | 16·50 |
| $C^{12}H^{12}O^2$ | 100 | 100 | 100·00 |

[May be regarded as $\left.\begin{matrix}C^{10}H^9O^2\\C^2H^3\end{matrix}\right\}$ or $\left.\begin{matrix}C^4H^3O^2\\C^8H^9\end{matrix}\right\}$].

## ¶ Amylomalic Acid.

$$C^{18}H^{16}O^{10} = C^{10}H^{12}O^2,C^8H^4O^8 = C^{10}H^{11}O,HO,C^8H^4O^8.$$

E. BREUNLIN. *Ann. Pharm.* 91, 323.

*Malamylic acid, Amyläpfelsaure.*

When 1 At. fusel-oil and 1 At. malic acid are digested together for some time at 120°, the malic acid gradually dissolves; the odour of the fusel-oil disappears; and the product, which is a viscid syrup while hot, solidifies on cooling in a white crystalline mass of the hydrated acid, which is soft and unctuous to the touch, melts at a gentle heat, and dissolves readily in water, alcohol and ether.

*Amylomalate of Ammonia.* Obtained by decomposing the lime-salt with carbonate of ammonia. Crystallizes only from a dilute alcoholic solution, in long needles united in concentric groups and having a diamond lustre.

| | | | Breunlin. |
|---|---|---|---|
| $NH^4O$ | 26 | 11·76 | 11·74 |
| $C^{10}H^{11}O$ | 79 | 35·75 | |
| $C^8H^4O^8$ | 116 | 52·49 | |
| $NH^4O,C^{10}H^{11}O,C^8H^4O^8$ | 221 | 100·00 | |

The *Potash* and *Soda-salts* do not crystallise, either from aqueous or from alcoholic solutions.

*Amylomalate of Baryta.* — A solution of amlyomalic acid saturated with carbonate of baryta, then filtered and evaporated, ultimately yields a thick, uncrystallisable syrup. On mixing a dilute aqueous solution of this syrup with alcohol, a bulky white precipitate is formed, which, after filtration, washing with alcohol, pressing, and drying in vacuo over oil of vitriol, becomes hard and brittle and may be pulverised. At 100° it melts into a resinous mass and obstinately retains water. After drying for some time at 100°, it gave by analysis 48·3 p. c. BaO, a quantity not agreeing with the formula $BaO,C^{10}H^{11}O,C^8H^4O^8$, which requires 28·26 p. c. BaO. — The aqueous solution of the salt heated with potash, gave off fusel-oil in considerable quantity.

*Amylomalate of Lime.* — When a warm dilute aqueous solution of amylomalic acid is saturated with chalk, and filtered hot, the filtrate solidifies on cooling in a white laminated crystalline mass, which may be purified by recrystallisation and pressure between bibulous paper. When dried in vacuo over oil of vitriol, it gives off water, and acquires a fatty lustre. At 100° it melts into a thick syrup.

| *Dried in vacuo over oil of vitriol.* | | | Breunlin. |
|---|---|---|---|
| CaO | 28 | 12·07 | 12·10 |
| 18 C | 108 | 46·55 | 46·06 |
| 16 H | 16 | 6·89 | 7·42 |
| 10 O | 88 | 34·49 | 34·42 |
| $CaO,C^{10}H^{11}O,C^8H^4O^8 + Aq$ | 240 | 100·00 | 100·00 |

The *lead-salt* is insoluble in water, and melts in hot water like the malate.

The other salts of amylomalic acid are all soluble in water; they do not give any conspicuous reactions. (Breunlin.) ¶.

## Amylotartaric Acid.

$$C^{18}H^{16}O^{12} = C^{10}H^{12}O^2,C^8H^4O^{10} = C^{10}H^{11}O,HO,C^8H^4O^{10}.$$

BALARD (1844.) *N. Ann. Chim. Phys.* 12, 309; also *J. pr. Chem.* 34, 141.
BREUNLIN. *Ann. Pharm.* 91, 314.

*Tartramylic acid, Amyltartersaure, Amylweinsäure.*

*Preparation.* 1. When fusel-oil is distilled with tartaric acid, a portion of the fusel-oil itself first passes over, then an acid and an ethereal product, and in the retort there remains a liquid which is syrupy after cooling, and characterised by intolerable bitterness. This liquid deposits, in the course of 24 hours, a white substance which does not behave like amylotartaric acid; the solution yields with carbonate of lime, unctuous, nacreous laminæ, which dissolve very abundantly in water, forming a solution from which a concentrated solution of nitrate of silver throws down the sparingly soluble silver-salt. (Balard.) — ¶. 2. When 150 pts.

of finely pulverised crystallised tartaric acid are digested for several days at about 130° with 88 pts. of rectified amylic alcohol, the tartaric acid gradually dissolves, the odour of the alcohol disappears, and a syrupy, yellowish liquid is formed, which by slow cooling solidifies in unctuous crystals united in warty masses. — These crystals have scarcely any odour of fusel-oil, but an extremely bitter taste. They melt at a gentle heat; dissolve very sparingly in a small quantity of water; and a larger quantity of water added to the solution separates the acid in oily drops. (Breunlin.)

The *Amylotartrates* are for the most part soluble in water. Most of them remain unaltered when their aqueous solutions are boiled, but they decompose when dried at 100°. (Breunlin.) Their formula is $C^{10}H^{11}MO^2, C^8H^4O^{10}$ or $MO, C^{10}H^{11}O, C^8H^4O^{10}$.

*Amylotartrate of Potash.* — By decomposing the baryta-salt, hydrated or anhydrous, with an aqueous solution of carbonate of potash, a filtrate is obtained which, on evaporation, and cooling, yields a white crystalline saline mass, easily purified by re-crystallisation. Gives off its water of crystallisation at 100°, and acquires a fatty lustre; the dry mass is with difficulty wetted by water. The crystals dissolve sparingly in cold, readily in boiling water. (Breunlin.)

| *Anhydrous.* | | | Breunlin. |
|---|---|---|---|
| KO | 47·2 | 18·28 | 18·14 |
| $C^{10}H^{11}O$ | 79·0 | 30·60 | |
| $C^8H^4O^{10}$ | 132·0 | 51·12 | |
| $C^{10}H^{11}KO^2,C^8H^4O^{10}$ | 258·2 | 100·00 | |

| *Hydrated.* | | | Breunlin. |
|---|---|---|---|
| $C^{10}H^{11}KO^2,C^8H^4O^{12}$ | 258·2 | 93·47 | 6·34 |
| 2 HO | 18·0 | 6·53 | |
| $C^{10}H^{11}KO^2,C^8H^4O^{12}$ + 2 Aq. | 276·2 | 100·00 | |

*Amylotartrate of Soda.* — Prepared like the potash-salt. The concentrated solution left to stand for some time in vacuo over oil of vitriol deposits soft nodular crystals, which are soluble in water, decompose at 100°, and are difficult to recrystallise. (Breunlin.)

| *Dried in vacuo.* | | | Breunlin. |
|---|---|---|---|
| NaO | 31·2 | 12·88 | 13·88 |
| $C^{10}H^{11}O$ | 79·0 | 32·62 | |
| $C^8H^4O^{10}$ | 132·0 | 54·50 | |
| $C^{10}H^{11}NaO^2,C^8H^4O^{10}$ | 242·2 | 100·00 | |

The excess of soda arises from contamination of the salt with carbonate of soda, an excess of which was used to decompose the baryta-salt.

*Amylotartrate of Baryta.*—*a. Anhydrous.* — When the aqueous solution of the acid is saturated while warm with carbonate of baryta, a thick viscid scum forms on the surface, containing amylotartrate of baryta, together with tartrate and carbonate. This substance, after being washed with water, is digested in hot alcohol which dissolves the amylotartrate. The solution does not yield any crystals, but on adding water to it, the

salt is precipitated in white amorphous flakes, which melt into a resinous mass at 100°. (Breunlin.)

| *Dried at* 100°. | | | Breunlin. |
|---|---|---|---|
| BaO | 76·6 | 26·63 | 26·43 |
| $C^{10}H^{11}O$ | 79·0 | 27·47 | |
| $C^8H^4O^{10}$ | 132·0 | 45·90 | |
| $C^{10}H^{11}BaO^2,C^8H^4O^{10}$ | 287·6 | 100·00 | |

This amorphous salt could not be converted into the crystallised salt *b*.

*b. Hydrated.* — The aqueous solution obtained by neutralising amylotartaric acid with carbonate of baryta, yields, when filtered and concentrated, colourless, nacreous, crystalline laminæ, which acquire a fatty lustre and become dull when dried at a gentle heat, and are decomposed at 100°. (Breunlin.)

| | | | Breunlin. |
|---|---|---|---|
| BaO | 76·6 | 25·07 | 25·45 |
| 18 C | 108·0 | 35·34 | 35·29 |
| 17 H | 17·0 | 5·56 | 5·41 |
| 13 O | 104·0 | 34·03 | 33·85 |
| $C^{10}H^{11}BaO^2,C^8H^4O^{10}$ + 2Aq | 305·6 | 100·00 | 100·00 |

*Amylotartrate of Lime.* — By mixing an alcoholic solution of the amorphous anhydrous baryta-salt with dilute sulphuric acid, neutralising the solution with carbonate of lime while water is gradually added, and evaporating the filtrate, first over the water-bath, then over oil of vitriol, a friable saline mass is obtained, which dissolves readily in water, and is not decomposed at 100°. (Breunlin.)

| | | | Breunlin. |
|---|---|---|---|
| CaO | 28 | 11·72 | 11·85 |
| $C^{10}H^{11}O$ | 79 | 33·05 | |
| $C^8H^4O^{10}$ | 132 | 55·23 | |
| $C^{10}H^{11}CaO^2,C^8H^4O^{10}$ | 239 | 100·00 | |

*Amylotartrate of Lead.* — A solution of the potash-salt mixed with acetate of lead, forms a bulky white precipitate very easy to filter and wash. After drying at 100°, it yielded 52 p. c. PbO; whereas the formula $C^{10}H^{11}PbO^2,C^8H^4O^{10}$ requires only 34·37 p. c.; hence the salt obtained as above must be either a basic salt or a mixture of several salts. (Breunlin.)

*Amylotartrate of Silver.* — When a hot concentrated solution of amylotartrate of potash is mixed with nitrate of silver, the liquid on cooling yields needles united in tufts and having a diamond lustre; they may be purified by washing with a small quantity of water and pressing between filtering paper. (Breunlin.) ¶. Balard precipitates the lime-salt with nitrate of silver (p. 80).

| | | | Balard. | Breunlin. |
|---|---|---|---|---|
| 18 C | 108 | 33·03 | 32·6 | 32·5 |
| 15 H | 15 | 4·59 | 4·6 | |
| Ag | 108 | 33·03 | 32·5 | |
| 12 O | 96 | 29·35 | 30·3 | |
| $C^{18}H^{15}AgO^{12}$ | 327 | 100·00 | 100·0 | |

## Valerate of Amyl.

$C^{20}H^{20}O^4 = C^{10}H^{11}O,C^{10}H^9O^3$.

BALARD. (1844.) *Ann. Chim. Phys.* 12, 315; also *J. pr. Chem.* 34, 143.
TRAUTWEIN. *Repert.* 91, 12.

*Baldrian-mylester, Ether valeriamylique.*—First obtained by Dumas and Stas, but regarded by them as valeraldide (p. 17), which is isomeric with it.—The so-called *Apple oil* used in perfumery consists of this compound. (Hofmann, *Ann. Pharm.* 81, 87.)

*Formation and Preparation.* 1. By distilling fusel-oil with valerianic acid. (Balard.) — 2. By adding to a cold-saturated solution of bichromate of potash, first oil of vitriol, then fusel-oil. (Dumas & Stas, Balard.)

*Properties.* Oily liquid, which boils at 196°, and has a vapour-density of 6·17. (Balard.)

| | | | Dumas & Stas. |
|---|---|---|---|
| 20 C | 120 | 69·77 | 70·07 |
| 20 H | 20 | 11·63 | 11·60 |
| 4 O | 32 | 18·60 | 18·33 |
| $C^{20}H^{20}O^4$ | 172 | 100·00 | 100·00 |

| | Vol. | Density. |
|---|---|---|
| C-vapour | 20 | 8·3200 |
| H-gas | 20 | 1·3860 |
| O-gas | 2 | 2·2186 |
| Vapour of $C^{20}H^{20}O^4$ | 2 | 11·9246 |
| | | 5·9623 |

*Decompositions.* When valerate of amyl is distilled with chromate of potash and sulphuric acid, part of it distils over unaltered, while the remainder is converted by oxidation into valerianic acid. (Trautwein). — 2. With aqueous potash, it yields valerianic acid and fusel-oil. (Balard.)

*Combinations.* The ether dissolves *phosphorus* and *iodine* in large quantity, but no sulphur even at the boiling heat. (Trautwein.)

It dissolves a few resins. (Trautwein.)

*Oxygen-nucleus.* $C^{10}H^8O^2$.

## Pyrotartaric Acid.

$C^{10}H^8O^8 = C^{10}H^8O^2,O^6$.

V. ROSE. *N. Gehl.* 3, 598.
FOURCROY & VAUQUELIN. *Ann. Chim.* 35, 161; also *Scher. J.* 5, 278. — *Ann. Chim.* 64, 42; also *N. Gehl.* 5, 713.
GOBEL. *N. Tr.* 10, 1, 26; also *Br. Arch.* 12, 74.
THEOD. GRUNER. *N. Tr.* 24, 2, 55.
PELOUZE. *Ann. Chim. Phys.* 56, 297; abstr. *J. pr. Chem.* 3, 54.

WENISELOS. *Ann. Pharm.* 15, 147.
AD. EDUARD ARPPE. *De Acido pyrotartarico,* Helsingforsiæ, 1847. Short abstr. *Ann. Pharm.* 66, 73.—Further: *Ann. Pharm.* 87, 228; abstr. *Pharm. Centr.* 1854, 106; *J. pr. Chem.* 62, 54; *Arch. ph. nat.* 25, 184.
SCHLIEPER. *Ann. Pharm.* 70, 121.

*Brenzweinsäure, brenzliche, branstige Weinsteinsäure, Acide pyrotartarique.*—Regarded as a peculiar acid by Guyton Morveau; pronounced to be pyro-acetic acid by Fourcroy & Vauquelin; again recognised as a peculiar acid by V. Rose, with whose opinion Fourcroy & Vauquelin afterwards agreed.

*Formation.* 1. By the dry distillation of tartaric acid, racemic acid, and cream of tartar. Perhaps in this manner;

$$2C^8H^6O^{12} = C^{10}H^8O^8 + 6CO^2 + 4HO.$$

*Preparation.* A. *From Tartaric acid.*—1. The best method is to fill a retort three-fourths with a pulverised mixture of equal parts of tartaric acid and pumice-stone (*comp.* x, 268), and raise the heat gradually so that the distillation may last 12 hours. The mass then swells up and yields a much larger quantity of pyrotartaric acid, so that the distillate crystallises when left at rest, and much less acetic acid and empyreumatic oil than when no pumice-stone is used. The pale yellow distillate is mixed with water; freed from the oil by means of a wet filter; evaporated till a crystalline film forms on the surface; set aside at 15°; the mother-liquor (which yields coloured crystals), allowed to drain from the resulting crystalline mass; this mass pressed between paper; and the aqueous solution poured into nitric acid, then heated and set aside, whereupon it yields perfectly pure crystals.—The coloured crystals obtained from the mother-liquor may likewise be spread out on several sheets of bibulous paper; a number of small basins filled with absolute alcohol placed around them; and a bell jar having its inner surface moistened with absolute alcohol, inverted over the whole; the alcoholic solution of the oil, with only a trace of acid, then soaks into the paper, and a snow-white, but still odorous acid remains. By solution in water and heating with nitric acid, this acid is rendered inodorous. By this process, 100 pts. of tartaric acid yield 7 to 8 pts. of pyrotartaric acid. (Arppe.)

2. Tartaric acid or cream of tartar (crude tartar yields nothing) is distilled alone in the dry state. From the watery distillate, which must be separated from the empyreumatic oil, and contains acetic and pyrotartaric acid (and pyroracemic acid, according to Berzelius), the pyrotartaric acid is either separated by repeated crystallisation and digestion with animal charcoal;—or the liquid is saturated with potash, and the pyrotartrate of potash purified by repeated crystallisation, digestion with animal charcoal, filtration, and subsequent distillation with dilute sulphuric acid, whereupon the pyrotartaric acid passes over, partly with the water, partly sublimed in needles. (V. Rose.)—Pulverised cream of tartar (which must be heated above 400°) does not swell up, but yields a large quantity of carbonic and acetic acid, together with, first a thin yellow, then a viscid brown oil, and an acid liquid containing a small quantity of pyrotartaric acid. Tartaric acid, on the contrary, swells up into a viscid mass, and froths over (and, according to Weniselos, yields no pyrotartaric acid, but if continually stirred with a platinum wire, behaves like cream of tartar. (Arppe.)—If the tartaric acid be distilled

at a temperature below 190°, the distillate yields, on evaporation, colourless crystals of pyrotartaric acid, which may be completely purified by means of charcoal; but if the distillation be carried on between 200° and 300°, the distillate, which is rich in empyreumatic oil, must be evaporated to a syrup in a retort; then distilled to dryness with a fresh receiver; and the resulting distillate exposed to a very low temperature, or evaporated in vacuo, whereupon it is resolved into empyreumatic oil and yellow crystals, which must be pressed between paper, and purified by digestion with animal charcoal and crystallisation. (Pelouze.) — To render the thus purified, but still yellowish acid, perfectly white, Göbel saturates it with carbonate of lime; evaporates the solution to dryness; extracts the empyreumatic oil from the residue by absolute alcohol; then dissolves it in boiling water; precipitates the lime by a proportional quantity of oxalic acid; then filters and evaporates. — Instead of carbonate of lime and oxalic acid, carbonate of baryta and sulphuric acid may be used. (Gruner.) — The acid which remains in the mother-liquor, and is contaminated with a large quantity of empyreumatic oil, cannot be decolorised with charcoal, but the colour may be removed by heating and evaporating it with a small quantity of fuming nitric acid. (Weniselos.) But this impure acid (not the pure acid) is decomposed by nitric acid. (Arppe.) — If the coloured acid be distilled till the residue is black and nearly dry, the nearly colourless crystalline acid which passes over, pressed between paper and dissolved in water, the solution poured into nitric acid, heated, and left to crystallise, and the crystals melted, the acid is obtained perfectly pure.

B. *From Sebacic acid.* — 1 pt. of sebacic acid and 30 pts. of nitric acid of sp. gr. 1·4 are digested for 8 days in such a manner that the greater part of the acid may run back into the flask; fresh nitric acid added from time to time as long as red fumes continue to escape; the residue diluted with an equal quantity of water, evaporated over the water-bath in a basin to a syrup, with continual addition of water, as long as nitric acid continues to escape; and the syrup set aside over oil of vitriol to crystallise. (Schlieper.)

*Properties.* Crystallises, either by sublimation or from water, in colourless four-sided needles (V. Rose); needles united in stars, and small laminæ united in spherical masses (Gruner); transparent, colourless, rhombic prisms, with acuminated ends, united in stars and spherules (Arppe); oblique rhombic prisms, truncated at the acute lateral edges. (Weniselos.) Melts at 100° (Gruner, Pelouze, Arppe); at 107° to 110° (Weniselos); solidifies in a radiated mass on cooling (Gruner); gives off white fumes a little above 100° (Gruner, Arppe); boils without decomposition at 140° to 150° (Weniselos); at 188°, with partial decomposition (Pelouze); begins to boil at 190°, the boiling point then gradually rising to 220° (Arppe), and may be sublimed without residue (V. Rose), in dendrites and stars (Weniselos), in shining needles (Schlieper). When pure, it is perfectly colourless (Gruner, Arppe); tastes very sour (Rose); like tartaric (Pelouze); or succinic acid (Schlieper).

| | | | Pelouze. | | Arppe. | Schlieper. |
|---|---|---|---|---|---|---|
| *Crystals dried in vacuo.* | | | *a.* | *b.* | *a.* | *c.* |
| 10 C | 60 | 45·46 | 45·86 | 46·38 | 45·55 | 45·35 |
| 8 H | 8 | 6·06 | 6·17 | 6·00 | 6·01 | 6·09 |
| 8 O | 64 | 48·48 | 47·97 | 47·62 | 48·44 | 48·56 |
| $C^{10}H^8O^8$ | 132 | 100.00 | 100·00 | 100·00 | 100·00 | 100·00 |

*a.* is the acid obtained from tartaric acid; *b.* from racemic, and *c.* from sebacic acid; the latter, solidified over oil of vitriol to a white, friable, somewhat glutinous mass, was analysed after fusion.

100 pts. of crystallised acid give off 8 pts. water between 90° and 100°, retaining their crystalline form but becoming turbid; 100 pts. of the crystallised acid mixed with 300 pts. of lead-oxide and with water, and evaporated, give off 8 pts. water between 90° and 100°, then 12·107 pts. more between 125° and 150°. (Gruner.) [No other chemist found the above 8 p. c. water of crystallisation.]

*Decompositions.* 1. The acid, when carefully heated in contact with the air, volatilises completely without decomposition (Schlieper); but when heated to the boiling point in a retort, it suffers partial decomposition, and yields, together with sublimed acid, a watery liquid containing acid, a yellow oil containing pyrotartaric acid, lighter than water, and having a sweet taste, (which however Weniselos denies,) and leaves in the retort a resin (Gruner), and ultimately charcoal (Weniselos). When pyrotartaric acid is kept for some time in a state of ebullition, whereupon it gives off vapours which excite coughing and smell somewhat like acetic acid, the residue crystallises but partially or not at all on cooling, and is found to be converted into oily anhydrous paratartaric acid ($C^{10}H^6O^6$), mixed with a certain quantity of unaltered pyrotartaric acid which gradually crystallises out. (Arppe.) — 2. The acid when heated strongly in contact with the air, turns brown, burns with a red-blue flame, and leaves a small quantity of easily combustible charcoal. (Gruner.) — Chlorine gas passed for a few hours through aqueous pyrotartaric acid, converts it, according to Gruner, into an acid exhibiting the reactions of citric acid; according to Weniselos, on the contrary, it exerts no action. — Hot strong nitric acid does not decompose pure pyrotartaric acid, but decomposes that which is contaminated with empyreumatic oil, &c. (Arppe.) Gruner obtained with an acid which was perhaps not quite pure, a small quantity of hydrocyanic acid, and a substance which coloured the liquid yellow. Weniselos likewise observed that the distillation of the acid mixture was attended with partial decomposition. — 3. Hot oil of vitriol carbonises pyrotartaric acid (Gruner), and its solution in dilute sulphuric acid likewise becomes coloured on boiling. (Arppe.) — 4. Pyrotartaric acid distilled with glacial phosphoric acid yields, first, pure anhydrous pyrotartaric acid, then also the hydrated acid; the residue however becoming carbonised. (Arppe.) — The acid is not decomposed by boiling with mercuric oxide or with nitrate of silver. (Göbel.)

*Combinations.* Pyrotartaric acid dissolves in 4 pts. of water at 12·5° (Göbel), in 3 pts. of water at 15° (Gruner), in 1½ pt. at 20° (Arppe). The solution does not decompose by keeping or by exposure to the sun (Weniselos), or by boiling (Arppe).

It dissolves in cold *oil of vitriol* without blackening. (Schlieper.)

*Pyrotartrates.*—The acid forms neutral or bibasic salts = $C^{10}H^6M^2O^2,O^6$, and acid or monobasic salts = $C^{10}H^7MO^2,O^6$. It has a great affinity for bases. All its salts are crystallisable (Arppe); they sustain a heat of 125° to 150° (most of them indeed of 200°, according to Arppe), but are decomposed between 250° and 300°. (Gruner.) In this decomposition the salts of the fixed alkalis give off water, then turn brown, froth up and give off gas, a yellow acid watery liquid, a thick stinking oil, and leave a carbonate of the alkali mixed with charcoal. The pyrotartrates

of the heavy metals likewise yield an acid watery distillate and an oily distillate. (Gruner.) The pyrotartrates, when heated in contact with the air, emit an offensive odour, and burn with a yellow smoky flame. (Gruner.) Heated with sulphuric acid, they yield a sublimate of pyrotartaric acid (V. Rose), and when heated with sulphuric acid and peroxide of manganese, they give off formic acid. (Gruner.) They are nearly all soluble in water, but dissolve very sparingly in alcohol, which rather precipitates them from their aqueous solution. (Arppe.)

*Pyrotartrate of Ammonia.* — *a. Bibasic,* $C^{10}H^6(NH^4)^2O^8$. — Formerly known only in the aqueous solution which, when evaporated, gives off ammonia and leaves the salt *b* (Arppe.) — ¶ Obtained by passing dry ammoniacal gas into a solution of pyrotartaric acid in alcohol of sp. gr. 0·80, whereupon the monobasic salt *b* first separates in delicate crystalline needles, and on continuing the passage of the gas, the crystalline mass re-dissolves almost entirely, and subsequently the neutral salt is deposited in the form of a white powder. — A better mode of preparation, however, is to pass the ammoniacal gas into the alcoholic solution of the acid, only till the acid salt is formed; then add alcohol saturated with ammonia, as long as a precipitate continues to form; then again pass the gas through till the solution becomes nearly transparent, and lastly saturate the liquid completely with ammoniacal gas after having poured it into another vessel. — This mode of proceeding precludes the possibility of the neutral salt being contaminated by any portion of the acid salt remaining undissolved. (Arppe.)

White powder, consisting of short microscopic prisms; smells slightly of ammonia when heated only a few degrees; between 90° and 100°, it gives off ammoniacal vapours, and is converted into the acid salt, which may be heated to 140° without further decomposition:

$$C^{10}H^6(NH^4)^2O^8 = C^{10}H^7(NH^4)O^8 + NH^3.$$

100 pts. of the neutral salt, heated to 115°, yielded 90·19 pts. of the acid salt; and 100 pts. heated to between 135° and 140°, yielded 88·94 pts. of the acid salt. By calculation the quantity should be 89·76 p. c. [166 : 149 = 100 : 89·76.] Hence it appears that a certain amount of decomposition takes place a little below 140°. — With potash, the salt gives off ammonia in considerable quantity. It dissolves very easily in water, sparingly in cold alcohol, and is decomposed by boiling alcohol, with evolution of ammonia and formation of the acid salt. (Arppe, *Ann. Pharm.* 87, 229.) ¶.

*b. Monobasic.* —Acute rhombohedrons, truncated even to the disappearance of the terminal edges. (Fig. 153.) Cleavage parallel to *p*. (Weniselos.) Small rhombic octohedrons and rhombic prisms, which assume a laminar appearance from shortening of their principal axis (Arppe); small four-sided needles. (Gruner.) The crystals are transparent (Gruner, Arppe); strongly acid (Weniselos), permanent in the air. (Gruner, Weniselos.) They do not give off any thing at 100°, but begin to decompose at 140°. (Arppe, *vid. sup.*) — ¶. The salt when heated in a distillatory apparatus, deliquesces to a viscid syrup at a temperature somewhat above 140°, giving off ammoniacal vapours; then assumes a darker colour and throws off bubbles: and at 150°, enters into a state of tranquil fusion. The residue then decomposes but slowly, not boiling till it becomes heated to 160°; the boiling point remains constant for a while at 176°; and rapid decomposition begins at 295°, a shining carbonaceous residue being left in the retort. The distillate consists at first of ammoniacal water, accompanied by a substance which crystallises out on

evaporation; afterwards there passes over an alkaline, then an acid oily liquid, which solidifies at 0° or when evaporated; and lastly a neutral oil which solidifies in the neck of the retort. The crystalline body which separates out during the entire operation is *bipyrotartramide* $C^{10}NH^7O^4$. (Arppe.)

$$C^{10}H^7(NH^4)O^8 - 4HO = C^{10}NH^7O^4. \quad ¶.$$

The crystals dissolve readily in water (Gruner), and with difficulty in boiling alcohol, whence they separate in the form of a crystalline powder on cooling. (Arppe.)

| | *Crystals.* | | Arppe. |
|---|---|---|---|
| 10 C | 60 | 40·27 | 40·03 |
| N | 14 | 9·39 | |
| 11 H | 11 | 7·39 | 7·39 |
| 8 O | 64 | 42·95 | |
| $C^{10}H^7(NH^4)O^8$ | 149 | 100·00 | |

*Pyrotartrate of Potash.*— *a. Bibasic.*— The aqueous acid exactly neutralized with carbonate of potash, and evaporated to a syrup, solidifies in flat prisms, which, in dry air, or at 25° even in damp air, give off water, swell up, and are converted into nodules consisting of microscopic needles. These crystals give off their 2 At. water at 200°; melt without decomposition at a temperature somewhat above 200°; and at a higher temperature, swell up and give off empyreumatic vapours. The dry salt, the nodules and the prisms all deliquesce in a cold damp atmosphere. The nodules, but not the anhydrous salt, dissolve in hot absolute alcohol, and the solution, deposits crystals on cooling; but from the saturated aqueous solution, alcohol precipitates the salt in oily drops. (Arppe.)

| | *a.* | | Arppe. | | *b.* | | Gruner. |
|---|---|---|---|---|---|---|---|
| 2 KO | 94·4 | 41·69 | 42·00 | 2 KO | 94·4 | 38·63 | 37·82 |
| $C^{10}H^6O^6$ | 114·0 | 50·36 | | $C^{10}H^6O^6$. | 114·0 | 46·64 | |
| 2 HO | 18·0 | 7·95 | 7·81 | 4 HO | 36·0 | 14·73 | 14·62 |
| $C^{10}H^6K^2O^8 + 2Aq$ | 226·4 | 100·00 | | + 4Aq | 244·4 | 100·00 | |

*a.* are the nodules dried over oil of vitriol within a bell-jar containing air; *b.* was obtained by Gruner in indistinct crystals, which were perhaps identical with Arppe's flat prisms.

*b. Monobasic.*— First observed by Fourcroy and Vauquelin, who compared it with cream of tartar, whereas Pelouze denies the existence of an acid potash-salt. Precipitated from the saturated solution of the salt *a* by pyrotartaric acid in the form of a crystalline powder. (Arppe.) One-half of a solution of pyrotartaric acid is exactly saturated with carbonate of potash, the other half then added, and the liquid evaporated. Large, transparent, oblique rhombic prisms. (Weniselos, Arppe.) They do not give off any thing at 200°, but when more strongly heated, they first give off acid, then swell up and evolve empyreumatic products. They dissolve in water somewhat less readily than the salt *a*, and with difficulty in boiling alcohol, which takes away a portion of the acid, and on the other hand throws down crystals from the saturated aqueous solution. (Arppe.)

| | *Crystals.* | | | Weniselos. | Arppe. |
|---|---|---|---|---|---|
| KO | 47·2 | .... | 27·73 | .... 26·56 | ........ 27·67 |
| $C^{10}H^7O^7$ | 123·0 | .... | 72·27 | | |
| $C^{10}H^7KO^8$ | 170·2 | .... | 100·00 | | |

*Pyrotartrate of Soda.*—*a. Bibasic.*—The acid saturated with carbonate of soda yields by slow evaporation, large crystalline laminæ with ragged edges, and by quick evaporation a syrup which solidifies in a crystalline mass on cooling. (Arppe.) Soft transparent needles united in spherules and permanent in the air. (Gruner.) The above-mentioned crystalline laminæ give off nearly all their water on exposure to the air and crumble to a white dust; give off all their water at 200°; and decompose at a stronger heat without fusion or intumescence. They dissolve readily in water, but not in alcohol, even at the boiling heat; alcohol indeed renders the aqueous solution turbid. (Arppe.)

| | *Needles.* | | Gruner. | | *Tables.* | | Arppe. |
|---|---|---|---|---|---|---|---|
| 2 NaO | 62·4 | 27·08 | 27·2 | 2 NaO | 62·4 | 21·94 | 21·84 |
| $C^{10}H^6O^6$ | 114·0 | 49·48 | | $C^6H^6O^6$ | 114·0 | 40·09 | |
| 6 HO | 54·0 | 23·44 | 20·9 | 12 HO | 108·0 | 37·97 | 37·90 |
| $C^{10}H^6Na^2O^8$ + 6Aq | 230·4 | 100·00 | | + 12Aq | 284·4 | 100·00 | |

*b. Monobasic.*—When the solution is evaporated over oil of vitriol within a bell-jar, there remains a dense crystalline mass consisting of microscopic rhombic prisms, which, after drying in the air, give off nothing at 200°, and contain 20·30 p. c. soda; therefore = $C^{10}H^7NaO^8$. (Arppe.) The salt dissolves readily in water. (Weniselos.)

A mixture of equal numbers of atoms of the bibasic potash and soda-salts leaves a gum when evaporated. (Arppe.)

*Pyrotartrate of Baryta.*—*a. Bibasic.*—When the warm aqueous acid is completely neuralized either by baryta-water or by carbonate of baryta, and the solution evaporated, the bibasic salt is deposited in the form of a white, shining, crystalline powder, which, when examined by the microscope, is found to consist of oblique rhombic needles. This crystalline powder begins to give off its water of crystallisation at 90°, parts with half of it at 100°, the whole at 160°, and undergoes no further decomposition at 200°. The crystalline powder dissolves readily in water either hot or cold, and is precipitated therefrom by alcohol. (Arppe.) Hence the clear aqueous mixture of chloride of barium and pyrotartaric acid or a soluble pyrotartrate, gives a precipitate in a few hours after the addition of alcohol and ammonia. (Arppe.)

| | *Crystalline powder.* | | | Arppe. | Gruner. |
|---|---|---|---|---|---|
| 2 BaO | 153·2 | .... | 50·53 | .... 50·61 | .... 49·70 |
| $C^{10}H^6O^6$ | 114·0 | .... | 37·60 | | |
| 4 HO | 36·0 | .... | 11·87 | .... 12·00 | .... 12·02 |
| $C^{10}H^6Ba^2O^8$ + 4Aq | 303·2 | .... | 100·00 | | |

*b. Monobasic.*—One-half of a portion of the aqueous acid is saturated with carbonate of baryta, then mixed with the other half and evaporated. It then effloresces and yields needles united in globular radiated

masses. These crystals soon become dull on exposure to the air, give off half their water at 90°, and the whole at 150°, leaving 92·74 p. c. of anhydrous salt, which at a stronger heat is converted into 61·38 p. c. of bibasic salt, and at a red heat, leaves 34·86 p. c. of carbonate of baryta. The needles give up half their acid to alcohol. They dissolve very readily in water. (Arppe.) — Weniselos obtained the salt in stars which were permanent in the air and reddened litmus.

| *Needles.* | | | Arppe. |
|---|---|---|---|
| BaO | 76·6 | 35·20 | 34·86 |
| $C^{10}H^7O^7$ | 123·0 | 56·53 | |
| 2 HO | 18·0 | 8·27 | 7·26 |
| $C^{10}H^7BaO^8$ + 2Aq | 217·6 | 100·00 | |

Arppe once obtained from an indefinite mixture of the acid and baryta-water, besides the above-mentioned needles, four and six-sided prisms which exhibited the same reactions as the needles, but contained 40·83 p. c. baryta.

*Pyrotartrate of baryta and potash*, and *Pyrotartrate of baryta and soda*, whose existence is maintained by Gruner, cannot really be obtained. (Arppe.)

*Pyrotartrate of Strontia.*— *a. Bibasic.*— The aqueous acid, neutralized by continued boiling with carbonate of strontia, yields after evaporation, small prisms easily soluble in water, and precipitated therefrom by alcohol. (Arppe.) Four-sided prisms sparingly soluble in water, insoluble in alcohol. (Gruner.)

| *Prisms air-dried.* | | | Arppe. | Gruner. |
|---|---|---|---|---|
| 2 SrO | 104 | 44·07 | 43·07 | 40·13 |
| $C^{10}H^6O^6$ | 114 | 48·30 | | |
| 2 HO | 18 | 7·63 | | 13·88 |
| $C^{10}H^6Sr^2O^8$ + 2Aq | 236 | 100·00 | | |

Gruner, according to his analysis, assigns to the salt 4 At. water.

*b. Monobasic.*—By digesting the dilute acid with carbonate of strontia and evaporating the filtrate, soft nacreous, microscopic laminæ are obtained which part with all their water at 130°, give off acid vapours at 135°, yield half their acid to alcohol, and are soluble in water. (Arppe.)

| *Laminæ.* | | | Arppe. |
|---|---|---|---|
| SrO | 52 | 26·94 | 26·43 |
| $C^{10}H^7O^7$ | 123 | 63·73 | |
| 2 HO | 18 | 9·33 | 9·39 |
| $C^{10}H^7SrO^8$ + 2Aq | 193 | 100·00 | |

*Pyrotartrate of Lime.*—*a. Bibasic.*—Precipitated on mixing the concentrated solutions of chloride of calcium and bibasic pyrotartrate of potash. By boiling the aqueous acid with carbonate of lime, till it is neutralized, evaporating the filtrate, and cooling, the salt is obtained in the form of a white crystalline powder, which, when examined by the microscope, is seen to consist of four-sided prisms. The salt gives off its water at 160°, but in other respects remains unaltered at 200°. It requires nearly 100 pts. of boiling water to dissolve it; dissolves readily in hydrochloric,

nitric or acetic acid; but is insoluble in alcohol. (Arppe.) The aqueous solution of the acid salt gives off part of its acid when evaporated, and deposits the bibasic salt in soft shining needles united in spherical masses, which give off their water when exposed to the air, and dissolve sparingly in water. (Gruner.)

| *Crystals.* | | | Arppe. |
|---|---|---|---|
| 2 CaO | 56 | 27·19 | 27·12 |
| $C^{10}H^6O^6$ | 114 | 55·34 | |
| 4 HO | 36 | 17·47 | 17·23 |
| $C^{10}H^6Ca^2O^8 + 4Aq$ | 206 | 100·00 | |

*b. With 3 At. Acid.*—The salt *a* dissolves readily in aqueous pyrotartaric acid, and the solution, when gently evaporated, yields crystals which give off their water at 110°, the acid then also beginning to evaporate. (Arppe.) The mono-acid salt cannot be obtained; for, on neutralising 1 pt. of the aqueous acid with lime and adding another 1 pt., a large quantity of bibasic salt is precipitated, and the remaining very acid liquid deposits on evaporation an additional quantity of bibasic salt, so that ultimately nothing but the pure acid is left. (Arppe.)

| *Crystals.* | | | Arppe. |
|---|---|---|---|
| CaO | 28 | 6·47 | 6·36 |
| $C^{10}H^7O^7$ | 123 | 28·40 | |
| 2 $C^{10}H^8O^8$ | 264 | 60·97 | |
| 2 HO | 18 | 4·16 | 4·77 |
| $C^{10}H^7CaO^8 + 2C^{10}H^8O^8 + 2Aq$ | 433 | 100·00 | |

*Pyrotartrate of Magnesia.*—*a. Monobasic.*—*a. Magnesia alba* dissolves very readily in the aqueous acid, forming a perfectly neutral liquid, which, when evaporated over oil of vitriol within a bell-jar containing air, leaves, first a viscid gum, then, after evaporation, an easily friable mass. This mass gives off water at 90°, but even at 170°, at which temperature further decomposition begins, it gives off only 24·41 p. c. in all. — *β*. When the above solution is evaporated merely to a syrup, and a small quantity of water added by drops, the syrup yields crystals, and is converted in a few hours into a dry crystalline mass, which, under the microscope, appears to consist of six-sided laminar prisms; it gives off nearly all its water at 130°, and the small remaining quantity at 200°, in all 40·57 p. c. — The salts *a* and *β* dissolve very readily in water, but are insoluble in alcohol which precipitates them from water; the aqueous solution of the salt *β* again yields crystals when evaporated; but that of the salt *a* leaves a syrup which does not crystallise till water is dropt into it. (Arppe.)

| *a. Dry gum.* | | | Arppe. |
|---|---|---|---|
| 2 MgO | 40 | 19·23 | 18·48 |
| $C^{10}H^6O^6$ | 114 | 54·81 | |
| 6 HO | 54 | 25·96 | 24·41 |
| $C^{10}H^6Mg^2O^8 + 6Aq$ | 208 | 100·00 | |

| *β. Crystalline mass.* | | | Arppe. |
|---|---|---|---|
| 2 MgO | 40 | 15·27 | 15·95 |
| $C^{10}H^6O^6$ | 114 | 43·51 | |
| 12 HO | 108 | 41·22 | 40·57 |
| $C^{10}H^6Mg^2O^8 + 12Aq$ | 262 | 100·00 | |

*b. Monobasic.* — Gummy. (Arppe.)

*Pyrotartrate of Glucina.*— The aqueous acid saturated with hydrate of glucina, leaves, when evaporated over oil of vitriol within a receiver containing air, the acid salt *b*, in the form of a mass which is viscid at first but afterwards becomes crystalline. This acid salt melts at 110°, gives off acid vapours, and at 180° leaves the neutral salt *a*. (Arppe.)

| | | *a.* | Arppe. | | | *b.* | Arppe. |
|---|---|---|---|---|---|---|---|
| 2 GO | 25·4 | 18·22 | 17·93 | GO | 12·7 | 4·71 | 4·70 |
| $C^{10}H^6O^6$ | 114·0 | 81·78 | | $C^{10}H^7O^7$ | 123·0 | 45·98 | |
| | | | | $C^{10}H^8O^8$ | 132·0 | 49·31 | |
| $C^{10}H^6G^2O^8$ | 139·4 | 100·00 | | $C^{10}H^7GO^8,C^{10}H^8O^8$ | 267·7 | 100·00 | |

*Pyrotartrate of Alumina.* — *a. Monobasic.*— 1. By boiling still moist hydrate of alumina with a quantity of aqueous acid less than sufficient to dissolve it, the salt is obtained in the form of a heavy powder insoluble in water. — 2. Precipitated in considerable quantity on mixing hydrochlorate of alumina with bibasic pyrotartrate of soda, in an excess of which it dissolves. (Arppe.)

| | | | Arppe. (1.) | Arppe. (2.) |
|---|---|---|---|---|
| $Al^2O^3$ | 51·4 | 28·03 | 27·26 | 27·30 |
| $C^{10}H^6O^6$ | 114·0 | 62·16 | | |
| 2 HO | 18·0 | 9·81 | 7·13 | 6·95 |
| | 183·4 | 100·00 | | |

*b. Acid.*— Hydrate of alumina, while still moist, dissolves slowly in the aqueous acid, and yields by evaporation, crystals, from which, when heated with water, 2 per cent. of hydrate of alumina separates. (Arppe.)

Green *Chromic Hydrate* dissolves sparingly in the boiling aqueous acid, and the green strongly acid solution yields by evaporation, green-spotted crystals of the acid; blue chromic hydrate forms with the cold aqueous acid, a blue solution, which becomes perfectly decolorised by evaporation to dryness. (Arppe.)

*Uranic Pyrotartrate.*—Bibasic pyrotartrate of potash added to uranic nitrate gradually throws down a white crystalline powder. (V. Rose.) The aqueous acid dissolves uranic hydrate so abundantly, that it loses its sour taste; and the yellow solution, when evaporated and cooled, deposits a yellow powder which becomes yellowish white when dry, dissolves readily in water, forming a yellow solution, and is precipitated therefrom in large quantity by alcohol in yellow flakes. Its aqueous solution, evaporated with a larger quantity of acid, leaves a crystalline mass. (Arppe.)

| *Precipitated by alcohol.* | | | Arppe. |
|---|---|---|---|
| 4 $U^2O^3$ | 576 | 59·26 | 59·45 |
| $C^{10}H^6O^6$ | 114 | 11·73 | |
| 2 $C^{10}H^7O^7$ | 246 | 25·31 | |
| 4 HO | 36 | 3·70 | 5·41 |
| $C^{10}H^6(2U^2O^2)O^8,2[C^{10}H^7(U^2O^2)O^8]$ + 4Aq | 972 | 100·00 | |

[As Arppe did not find the loss of weight to amount to 5·41 p. c. till he heated the salt to 200°, it is possible that acid may have passed off with the water.]

*Pyrotartrate of Manganese.*—Carbonate of manganese dissolves slowly in the cold aqueous acid, quickly in the same when hot, forming a not perfectly neutral liquid, which leaves a gum when evaporated. This gum still retains 2 At. water at 200°, and decomposes at a stronger heat before the water escapes. It dissolves readily in water, and is precipitated therefrom by alcohol, as a curdy mass, which diffuses itself in a larger quantity of alcohol, in the form of a reddish, heavy, granular powder. (Arppe.)

| At 200°. | | | Arppe. | | | | Arppe. |
|---|---|---|---|---|---|---|---|
| 2 MnO | 72 | 35·30 | 34·90 | 2 MnO | 72 | 30 | 29·80 |
| $C^{10}H^6O^6$ | 114 | 55·88 | | $C^{10}H^8O^8$ | 132 | 55 | |
| 2 HO | 18 | 8·82 | | 4 HO | 36 | 15 | 14·61 |
| $C^{10}H^6Mn^2O^8 + 2Aq$ | 204 | 100·00 | | + 6Aq | 240 | 100 | |

Antimonic oxide is quite insoluble in the aqueous acid (Arppe), or dissolves very sparingly. (Gruner.)

*Pyrotartrate of Bismuth.*— The heated acid does not dissolve the oxide or the carbonate of bismuth, and but sparingly the recently precipitated hydrate. The solution saturated as completely as possible, becomes turbid when boiled and clear again on cooling. When evaporated, it leaves the crystallised acid and a gummy substance. With water it forms a precipitate, which increases when the liquid is heated, and diminishes on further addition of water. The same precipitate is formed by alcohol. The precipitate ignited in a glass tube, leaves a residue which, if exposed to the air while yet warm, takes fire and burns away, leaving oxide of bismuth. (Arppe.)

| | | | Arppe. | |
|---|---|---|---|---|
| *Air-dried precipitate.* | | | *a.* | *b.* |
| 4 $Bi^2O^3$ | 948 | 71·49 | 71·54 | 71·15 |
| 3 $C^{10}H^6O^6$ | 342 | 25·79 | | |
| 4 HO | 36 | 2·72 | 2·66 | 2·78 |
| $C^{10}H^6(2Bi^2O^2)O^8,2[C^{10}H^7(Bi^2O^2)O^8] + 2Aq$ | 1326 | 100·00 | | |

*a* was obtained with water; *b*, with alcohol.

*Pyrotartrate of Zinc.*—*a. Polybasic.*— When the somewhat acid solution of *b* is evaporated to a soft gum and redissolved in water, there remains a small quantity of powder containing 55 per cent. of zinc oxide. (Arppe.)

*b. Bibasic. α. Anhydrous.*— The metal dissolves slowly in the acid, the oxide quickly at a boiling heat. The syrup obtained by evaporating the acid filtrate, forms with alcohol a curdy coagulum, which soon changes to a granular powder and dissolves in water, leaving a small quantity of the salt *a*. But by precipitating a very acid solution with alcohol, a very soft powder is obtained, which dissolves completely in cold water, forming a solution which becomes turbid when boiled. Vid. analysis *b*, *α*.

*β. Hydrated.* — Carbonate of zinc disolves very rapidly in the hot acid; and the nearly neutral solution leaves on evaporation, a thick syrup which gradually forms granules, and on addition of a small quantity of water, is completely converted into a mass which is soluble in water, and

must be pressed between paper; at 200°, it gives off 14·99 p. c. or 4 At. water, retaining 2 At. (Arppe.)

| *b, α. Air-dried.* | | | Arppe. | *b, β. Air-dried.* | | | Arppe. |
|---|---|---|---|---|---|---|---|
| 2 ZnO | 80·4 | 41·36 | 41·53 | 2 ZnO | 80·4 | 32·37 | 32·73 |
| $C^{10}H^6O^6$ | 114·0 | 58·64 | | $C^{10}H^6O^6$ | 132·0 | 53·14 | |
| | | | | 4 HO | 36·0 | 14·49 | 14·99 |
| $C^{10}H^6Zn^2O^8$ | 194·4 | 100·00 | | + 6Aq | 248·4 | 100·00 | |

*Pyrotartrate of Cadmium.* — *a. Bibasic.* — *α.* With 4 At. water. — From the acid saturated with carbonate of cadmium, alcohol throws down a salt, which, after drying in the air, gives off 2 At. water at 100°, and the other two near the point at which it decomposes. (Arppe.)

*β. With* 6 *At. water.* — The acid saturated with oxide, hydrated oxide, or carbonate of cadmium and evaporated to a thick syrup, gradually yields granules, and then, after being covered with a little water, and left to evaporate in dry air, solidifies almost entirely to a powder, which is freed from the acid mother-liquor by pressure between paper. It is quite neutral, gives off 12·73 p. c. (4 At.) water at 200°, near its decomposing point, retaining therefore 2 At. It dissolves readily in water, and is precipitated from the solution by alcohol. (Arppe.) — The acid solution yields small four-sided prisms, which dissolve readily in water, contain 48·48 p. c. cadmic oxide after drying at 130°, and 32 p. c. after drying at 100°. Alcohol abstracts acid from them, so that neutral salt remains. (Gruner.)

| *a, α. Air-dried.* | | | Arppe. | *a, β. Air-dried.* | | | Arppe. |
|---|---|---|---|---|---|---|---|
| 2 CdO | 128 | 46·04 | 45·91 | 2 CdO | 128 | 43·24 | 43·13 |
| $C^{10}H^6O^6$ | 114 | 41·01 | | $C^{10}H^6O^6$ | 132 | 44·60 | |
| 4 HO | 36 | 12·95 | 12·67 | 4 HO | 36 | 12·16 | 12·67 |
| $C^{10}H^6Cd^2O^8$ + 4Aq | 278 | 100·00 | | + 6Aq | 296 | 100·00 | |

*b. Monobasic.*— The solution of the salt *a*, mixed with as much acid as it already contains, leaves on evaporation, a viscid mass in which a few long slender needles gradually form. (Arppe.)

*Stannous Pyrotartrate.*— The acid does not dissolve metallic tin, but dissolves the protoxide and its hydrate with facility. The solution filtered from a yellow basic salt, becomes very turbid when mixed with water, and forms with alcohol a copious precipitate, which, after drying at 200°, contains 70·16 p. c. stannous oxide, and is therefore $2SnO,C^{10}H^6Sn^2O^8$; it is decomposed by boiling water, with solution of only a very small portion. (Arppe.)

*Pyrotartrate of Lead.*— *a. Sexbasic.*—Obtained by treating the salt *b* with ammonia and washing with water, which does not dissolve any of the lead. (Arppe.)

*b. Quadribasic.*— The free acid or the bibasic potash-salt forms with basic acetate of lead a white curdy precipitate, soluble in acids and in excess of subacetate of lead, but insoluble in water. (Pelouze.) The curdy precipitate obtained with the ammonia-salt, and soluble in pyro-

tartaric acid, cakes together in a few hours on the bottom of the vessel, forming a hard, yellowish white, friable crust. (Schlieper.)

| *Salt a. at* 200°. | | | | Arppe. |
|---|---|---|---|---|
| 6 PbO | 672 | .... 85·50 | ........ | 85·40 |
| $C^{10}H^6O^6$ | 114 | .... 14·50 | | |
| 4 PbO,$C^{10}H^6Pb^2O^8$ | 786 | .... 100·00 | | |

| *Salt b. at* 100°. | | | | Arppe. |
|---|---|---|---|---|
| 4 PbO | 448 | .... 79·71 | ........ | 79·66 |
| $C^{10}H^6O^6$ | 114 | .... 20·29 | | |
| 2 PbO,$C^{10}H^6Pb^2O^8$ | 562 | .... 100·00 | | |

Schlieper's salt described under *b* contains at 100° only 72·97 p. c. of oxide of lead. By treating the salt *c* with ammonia, Gruner obtained a white powder, which contained at 130°, 76·55 p. c. lead-oxide and 3·09 p. c., water, and is therefore 2PbO,$C^{10}H^6Pb^2O^8$ + 2Aq.

*c. Bibasic.*— The free acid does not precipitate nitrate or neutral acetate of lead (Pelouze); it precipitates neutral acetate of lead after a while in bundles of needles (Fourcroy & Vauquelin, Weniselos); basic acetate of lead precipitates the same salt. (Arppe.) The bibasic potash-salt forms with neutral acetate of lead in a few hours, crystalline nodules (V. Rose), white flakes, containing 66·05 p. c. oxide (Pelouze); if alcohol be added, the precipitation takes place immediately,—and with nitrate of lead, after a while, needles. (Weniselos.) By boiling the acid with lead-oxide, filtering from a basic salt, and evaporating and cooling, the salt is likewise obtained in needles, which however, according to Arppe (not, according to Gruner) are anhydrous. The needles lose their transparency on exposure to the air. (Gruner.) The salt melts on heating the liquid from which it has been precipitated, and forms oily drops. (Schlieper.) It yields by dry distillation, empyreumatic oil and a watery liquid containing acetic acid, and, when heated in contact with the air, gives off acid vapours, takes fire and then burns away with a glimmering light, even after the fire has been removed. (Gruner.) It dissolves very sparingly in cold water (Weniselos), more readily in hot water, from which it crystallises out on cooling; the solution of the precipitate in excess of nitrate of lead also yields four-sided needles. (Arppe.)

| *Air-dried crystals* | | | | Gruner. | | Arppe. |
|---|---|---|---|---|---|---|
| 2 PbO | 224 | .... 59·89 | ........ | 59·02 | .... | 59·73 |
| $C^{10}H^6O^6$ | 114 | .... 30·48 | | | | |
| 4 HO | 36 | .... 9·63 | ........ | 9·58 | .... | 9·65 |
| $C^{10}H^6Pb^2O^8$ + 4Aq. | 374 | .... 100·00 | | | | |

*Ferrous Pyrotartrate.*— The acid, especially when hot, dissolves iron with evolution of hydrogen. The solution reddens quickly, and forms red flakes with water or alcohol. (Arppe.)

*Ferric Pyrotartrate.*— *a. With* 18 *At. Base.*— Obtained by treating either of the following salts with excess of ammonia and washing. Has the appearance of hydrated ferric oxide. After drying at 100°, it gives off 10·48 p. c. water at 200. (Arppe.)

*b. Sexbasic.* — Ferric hydrochlorate saturated with ammonia as far as possible without permanent precipitation, forms with bibasic pyrotartrate of soda, a copious precipitate, which, after washing and drying at 100°, appears hard and friable, gives off 8·49 p. c. water at 200°, is insoluble in water, very sparingly in acetic acid, but dissolves abundantly in nitric acid. (Arppe.)

| *Salt a. dried at* 100°. | | | Arppe. |
|---|---|---|---|
| 18 $Fe^2O^3$ | 1440 | 83·92 | 82·94 |
| $C^{10}H^6O^6$ | 114 | 6·64 | |
| 18 HO | 162 | 9·44 | 10·48 |
| | 1716 | 100·00 | |

| *Salt b. dried at* 100°. | | | Arppe. |
|---|---|---|---|
| 6 $Fe^2O^3$ | 480 | 74·08 | 74·27 |
| $C^{10}H^6O^6$ | 114 | 17·59 | |
| 6 HO | 54 | 8·33 | 8·49 |
| | 648 | 100·00 | |

In the salt *a*, Arppe assumes 20 Aq, which certainly agrees better with the analysis.

*c. With* $\frac{4}{3}$ *At. Base.* — Ferric hydrochlorate mixed with ammonia till a reddish colour just begins to appear, forms with bibasic pyrotartrate of soda, a red precipitate which has a gummy consistence only when warm. This precipitate washed, first with water containing sal-ammoniac, then with pure water, and afterwards dried, appears brown, gives off 7·86 p. c. water at 200°, and, when moistened with water, assumes a yellowish brown colour, does not become gummy, and scarcely colours the water. (Arppe.)

| *Dried at* 100°. | | | Arppe. |
|---|---|---|---|
| 4 $Fe^2O^3$ | 320 | 44·69 | 44·64 |
| 3 $C^{10}H^6O^6$ | 342 | 47·77 | |
| 6 HO | 54 | 7·54 | 7·86 |
| | 716 | 100·00 | |

*d. Monobasic.* — 1. Sesquichloride of iron free from excess of acid, is precipitated by the bibasic soda-salt; the red, very gummy precipitate collected on a filter after addition of sal-ammoniac, without which the liquid will not filter well; and washed by decantation after drying, because, if water were immediately poured upon it, it would become pitchy and stop up the filter. It is brown in the dry state, but red and gummy when moist. It dissolves sparingly in cold water (in 200 pts. according to Pelouze), forming a clear liquid, which, in a few days, solidifies to a stiff mass. (Arppe.) 2. The solution of recently precipitated ferric hydrate in the boiling acid, if exhausted with alcohol, after evaporation to dryness, leaves a red, gummy residue of the same salt which turns brown after drying.

| *Air-dried.* | | | Arppe (1). | Arppe (2). |
|---|---|---|---|---|
| $Fe^2O^3$ | 80 | 33·47 | 33·01 | 33·51 |
| $C^{10}H^8O^8$ | 132 | 55·23 | | |
| 3 HO | 27 | 11·30 | 12·65 | 11·07 |
| | 239 | 100·00 | | |

The 12·65 and 11·07 p. c. water escape at 100°, but no more. (Arppe.)

*e. With* 9 *At. acid.*— The concentrated acid dissolves recently precipitated ferric hydrate pretty easily (not the dry), forming a reddish yellow, very acid liquid which soon changes completely to a yellow crystalline mass. This mass melts at 105°, giving off 1·81 p. c. water, and after evolving acid vapours, ultimately leaves 6·02 p. c. ferric oxide. It is therefore perhaps $Fe^2O^3,9C^{10}H^6O^6$, 18 Aq., and the loss at 105° amounts to 3 Aq. On exhausting the crystalline mass with absolute alcohol, there remains a brick-red powder, which is likewise insoluble in water, contains 31·99 p. c. ferric oxide at 200°, and is therefore $2Fe^2O^3,3C^{10}H^6O^6$. (Arppe.) By evaporating and cooling the brown solution of the hydrated oxide in the acid, Gruner obtained brown transparent needles, permanent in the air.

*Pyrotartrate of Cobalt.*— *a. Basic.* — By exhausting the salt *b* with alcohol and washing the residue with water. Rose-coloured salt, which when heated gives off water, to the amount of 17·27 p. c. at 200°, and turns blue; it contains 63·25 p. c. water. (Arppe.)

*b. Acid.*— Hydrated protoxide of cobalt dissolves sparingly in the acid, forming a strongly acid liquid, which on evaporation deposits colourless crystals of the acid mixed with a sparingly soluble red salt. On neutralizing with ammonia, there is obtained a rose-coloured crystalline powder containing ammonia, and dissolving with decomposition in water. (Arppe.)

*Pyrotartrate of Nickel.*— *a. Bibasic.* — The hydrate dissolves very easily in the acid. On evaporating the green solution to a crystalline mass, and exhausting the residue completely with alcohol, there remains a green crystalline powder very sparingly soluble in water. This powder, after drying in the air, gives off 11·62 p. c. water at 200°, and a little above that temperature, it slowly parts with the remainder, amounting in all to 15·89 p. c. without further decomposition. (Arppe.)

| *Air-dried.* | | | Arppe. |
|---|---|---|---|
| 2 NiO | 75 | 33·33 | 33·50 |
| $C^{10}H^6O^6$ | 114 | 50·67 | |
| 4 HO | 36 | 16·00 | 15·89 |
| $C^{10}H^6Ni^2O^8$ + 4Aq | 225 | 100·00 | |

*b. Bi-acid.*— The solution of the hydrated oxide in the acid leaves, when evaporated under a bell-jar with oil of vitriol, first a syrup, then a crystalline mass, which melts at 115° and gives off 2·85 p. c. water, but emits acid vapours even at 120; in the free state, but not when dissolved in water, it is decomposed by alcohol and yields the salt *a*. (Arppe.)

| *Crystalline mass.* | | | Arppe. |
|---|---|---|---|
| NiO | 37·5 | 12·08 | 11·90 |
| 2 $C^{10}H^6O^6$ | 228·0 | 73·43 | |
| 5 HO | 45·0 | 14·49 | |
| $C^{10}H^7NiO^8,C^{10}H^8O^8$ + 2Aq | 310·5 | 100·00 | |

*Cupric Pyrotartrate.* — *a. Quadribasic.* —When the azure-coloured solution of the salt *b* in ammonia is evaporated with addition of water, it becomes nearly decolorized and deposits greenish flakes, which after

drying in the air contain 51·40 p. c. cupric oxide and are therefore $4CuO,C^{10}H^{6}O^{6}$, 4Aq. (Arppe.)

*b. Bibasic.* — 1. The warm acid forms with cupric oxide, a pale green salt, part of which remains dissolved in the excess of acid, forming a green solution, which, when evaporated, deposits green crystals of the salt together with crystals of the acid. (Gruner).— 2. The bibasic soda-salt, but not the free acid, precipitates cupric salts bluish green. (V. Rose, Arppe), blue (Göbel), bluish (Weniselos).— The air-dried salt gives off its water at 130°, and at a higher temperature emits vapours having a strong odour of butyric acid. (Arppe.) The salt subjected to dry distillation appears to yield formic acid. (Gruner.) It dissolves in about 230 pts. of water (Pelouze), easily in acids and ammonia, scarcely in alcohol. (Arppe.)

| | *Dried at* 100°. | | Göbel (2). |
|---|---|---|---|
| 2 CuO | 80 | 37·73 | 37·76 |
| 10 C | 60 | 28·30 | 28·40 |
| 8 H | 8 | 3·78 | 2·84 |
| 8 O | 64 | 30·19 | 31·00 |
| $C^{10}H^{6}Cu^{2}O^{8}$ + 2Aq | 212 | 100·00 | 100·00 |

| | *Air-dried.* | | Gruner (1). | Arppe (2). |
|---|---|---|---|---|
| 2 CuO | 80 | 34·77 | 34·18 | 34·57 |
| $C^{10}H^{6}O^{6}$ | 114 | 49·58 | | |
| 4 HO | 36 | 15·65 | 15·40 | 15·60 |
| $C^{10}H^{6}Cu^{2}O^{8}$ + 4Aq | 230 | 100·00 | | |

The blue solution of the salt *b* in ammonia leaves, when evaporated under a bell-jar, first a thick syrup, then a dry mass, which contains 86·41 p. c. of the dry salt *b*, and is therefore $C^{10}H^{6}Cu^{2}O^{8},NH^{4}O$. (Arppe.)

*Mercurous Pyrotartrate.* —The bibasic potash-salt, (not the free acid, according to Pelouze), forms an abundant precipitate with mercurous nitrate. (V. Rose.) The dried white pulverulent salt contains 74·81 p. c. mercurous oxide. In the moist state, it turns grey when exposed to the sun. When heated, it sublimes partly undecomposed and leaves charcoal. (Harff.) It is nearly insoluble in water, easily soluble in nitric acid, somewhat in aqueous bibasic pyrotartrate of soda (Arppe), insoluble in alcohol and ether. (Harff, *N. Br. Arch.* 5, 274.)

The salt when suspended in water, is converted by ammonia, into a velvet-black, tasteless powder containing ammonia and 86·8 p. c. mercurous oxide. (Harff.)

*Mercuric Pyrotartrate.*— 1. The solution obtained by digesting mercuric oxide with the acid, yields on evaporation, a transparent, non-crystalline mass, from which cold water throws down a white powder. This powder redissolves when heated, and yields crystalline nodules on cooling. (Gruner.) The hot-filtered solution of mercuric oxide in the concentrated acid deposits a white powder on cooling. (Harff.) The solution of mercuric oxide in the boiling acid, when evaporated by heat, becomes turbid on cooling, and forms with water a precipitate which disappears on heating the liquid; the solution evaporated under a bell-jar leaves a mass consisting of very small globules or grains. (Arppe.)

2. The potash-salt (not the free acid, according to V. Rose) added to a solution of mercuric nitrate, throws down a white crystalline powder, having a metallic taste, and containing 60·18 p. c. mercuric oxide. This powder is decomposed by dry distillation, leaving a residue of charcoal; dissolves in 119 pts. of water, forming a solution which deposits a basic salt on boiling; it dissolves more readily in acidulated water, and in oil of vitriol, especially when warm; but is nearly insoluble in alcohol and ether. (Harff, *N. Br. Arch.*, 5, 276.) Corrosive sublimate forms with the soda-salt a scanty precipitate agreeing in composition with that obtained by (1). (Arppe.) Corrosive sublimate forms with the acid, a white precipitate which disappears on agitation; then, after 12 hours a brown red precipitate; with the potash-salt, it gradually forms a white cloud, and then after 12 hours, a brown precipitate. (Göbel.)

The salt suspended in water is converted by ammonia into a white powder, which has a faint metallic taste, contains 77·9 p. c. mercuric oxide and gives off ammonia when treated with potash. (Harff.)

*Pyrotartrate of Silver.* — Bibasic pyrotartrate of potash (ammonia, according to Schlieper; soda, according to Arppe) precipitates nitrate of silver immediately and abundantly. (V. Rose.) The white precipitate resembles flakes of hydrate of alumina, and slowly dries up to hard translucent lumps which yield a brown-white powder. (Schlieper.) Under the microscope, it is seen to consist of delicate needles; in the moist state it turns grey on exposure to light (poppy-blue according to Göbel), gives off, when strongly heated, vapours smelling of butyric acid, and dissolves sparingly in cold water, readily in nitric acid, acetic acid, and ammonia. (Arppe.) — The free acid forms with nitrate of silver, after 12 hours, a grey precipitate (Fourcroy and Vauquelin), and with acetate of silver, after 12 hours, a black-brown precipitate. (Göbel.)

| *Dried at* 100°. | | | Schlieper. | Arppe. |
|---|---|---|---|---|
| 10 C | 60 | 17·34 | 18·61 | 17·36 |
| 6 H | 6 | 1·74 | 2·01 | 1·88 |
| 2 Ag | 216 | 62·43 | 60·27 | 62·29 |
| 8 O | 64 | 18·49 | 19·11 | 18·47 |
| $C^{10}H^6Ag^2O^8$ | 346 | 100·00 | 100·00 | 100·00 |

The soda-salt forms with bichloride of *platinum*, a scanty red-brown precipitate, which quickly changes to metallic platinum. (Arppe.)

Pyrotartaric acid dissolves readily in *alcohol* and *ether*. (Arppe.)

The empyreumatic oil which passes over in the dry distillation of tartaric acid, contains an acid different from pyrotartaric acid, which crystallises in three or four-sided needles, precipitates hydrochlorate and sulphate of lime after a while in the crystalline form, and forms copious precipitates with neutral acetate of lead and mercurous and mercuric nitrates (not with nitrate of silver). (V. Rose.)

Gruner likewise observed a peculiar acid which crystallised like benzoic acid, volatilised readily in pungent vapours, but boiled when quickly heated, turning brown and leaving a large quantity of charcoal.

*Conjugated Compounds of the Oxygen-nucleus* $C^{10}H^8O^2$.

## Pyrotartrate of Methyl.

$C^{14}H^{12}O^8 = 2C^2H^3O,C^{10}H^6O^6$. ?

The solution of pyrotartaric acid in wood-spirit, saturated with dry hydrochloric acid and distilled over chloride of calcium and carbonate of magnesia, yields a yellowish oil which sinks in water. (Arppe.)

## Pyrotartrate of Ethyl.

$C^{18}H^{16}O^8 = 2C^4H^5O,C^{10}H^6O^6$.

Gruner (1832) and Arppe in the memoirs cited on pages 83, 84.
Malaguti. *Ann. Chim. Phys.* 64, 275; also *Ann. Pharm.* 25, 272; als *J. pr. Chem.* 11, 225.

*Preparation.* — A mixture of 1 pt. concentrated hydrochloric acid, 2 pts. pyrotartaric acid, and 4 pts. alcohol, is distilled to one-half; and the oily pyrotartrate of ethyl precipitated from the acid residue by water, washed repeatedly with water, digested with lead-oxide, and distilled. (Gruner.) 2. The solution of pyrotartaric acid in absolute alcohol is saturated with dry hydrochloric acid; evaporated a little; the compound ether precipitated by water in the form of a yellow oil; and this oil, after the watery liquid has been decanted, is neutralised with carbonate of soda, dried over chloride of calcium, and rectified. (Arppe.) — 3. The same process as for citric ether, excepting that hydrochloric acid is to be used in place of sulphuric, and the ether purified by distillation, — whereby it is but slightly decomposed,—and washing. (Malaguti.)

*Properties.* Transparent, colourless oil (yellow, according to Gruner); of sp. gr. 1·016 at 185°; begins to boil at 218°, but the boiling point rapidly rises in consequence of partial decomposition; smells like *calamus aromaticus;* has a pungent bitter taste (and burning, according to Gruner); neutral (Malaguti).

| | | | Malaguti. | Arppe. |
|---|---|---|---|---|
| 18 C | 108 | 57·45 | 57·43 | 57·40 |
| 16 H | 16 | 8·51 | 8·67 | 8·71 |
| 8 O | 64 | 34·04 | 33·90 | 33·89 |
| $C^{18}H^{16}O^8$ | 188 | 100·00 | 100·00 | 100·00 |

*Decompositions.* 1. The ether is not set on fire by the flame of a candle, but burns with a white flame when more strongly heated. It is scarcely attacked by chlorine, iodine or bromine. — 2. It is decomposed by nitric acid, but only with the aid of heat. — 3. Dissolves, with slow decomposition in cold oil of vitriol, and when heated therewith, quickly produces sulphurous acid and charcoal. The solution in hydrochloric acid likewise decomposes at 80°. (Malaguti.) — 4. It is slowly decomposed by water, more quickly by aqueous potash, into alcohol and pyrotartaric

acid. (Gruner, Malaguti.) Dry ammoniacal gas has no action upon it; and no precipitate is produced by baryta, strontia, or lime-water. — (Malaguti.)

*Combinations.* — The ether is nearly insoluble in water, dissolves readily in cold oil of vitriol and hydrochloric acid, and in all proportions in ether and alcohol, being precipitated from the latter by water. — (Gruner.)

*Oxygen nucleus* $C^{10}H^6O^4$.

## Anhydrous Pyrotartaric Acid.

$C^{10}H^6O^6 = C^{10}H^6O^4,O^2$.

ARPPE. (1847.) *De acido pyrotartarico, &c.* 20.

*Pyrotartaric Anhydride, Brenzweinanhydrid.*

*Formation.* 1. Pyrotartaric acid when boiled for some time, loses its crystallisability, being for the most part converted into the oily anhydrous acid, and if then distilled, yields, first water, then the anhydrous acid mixed with a small portion of the ordinary acid. — 2. Pyrotartaric acid distilled with phosphoric acid, yields a distillate which, so long as no carbonisation takes place, consists of the pure anhydrous acid.

*Preparation.* 1. Fused pyrotartaric acid mixed with glacial phosphoric acid is distilled till the residue begins to turn brown, pure anhydrous pyrotartaric acid passing over all the while; the portion of the mixture which remains liquid after cooling is then decanted into another retort, and about two-thirds distilled off at about 190°.

*Properties.* — Colourless oil, which does not solidify at — 10°, sinks in water, boils at 230°, and volatilises undecomposed; inodorous at 20°, smells like acetic acid at 40°; excites first a sweetish then a sour taste like that of the hydrated acid; when swallowed, it produces a burning and scratching sensation in the throat. Perfectly neutral.

| | | | Arppe. |
|---|---|---|---|
| 10 C | 60 | 52·63 | 52·65 |
| 6 H | 6 | 5·26 | 5·20 |
| 6 O | 48 | 42·11 | 42·15 |
| $C^{10}H^6O^6$ | 114 | 100·00 | 100·00 |

*Decomposition.* Converted slowly by water, quickly by aqueous alkalis, into ordinary pyrotartaric acid.

*Combinations.* Dissolves very sparingly in *water*, readily in *alcohol*, whence it is precipitated by water in oily drops, which gradually change into the hydrated acid. (Arppe.)

*Appendix to Pyrotartaric Acid.*

## ¶. Bipyrotartramide $C^{10}H^7NO^4$.

ARPPE. *Ann. Pharm.* 87, 231.

*Bipyrtramide, Pyrotartrimide.*

Obtained by the dry distillation of acid pyrotartrate of ammonia (p. 87). To purify the crystalline product, which separates during the whole course of the operation, it is thoroughly moistened with water, dissolved by the aid of heat, left to separate by cooling, and pressed; and these operations are repeated till the yellowish colour is quite and the empyreumatic odour nearly gone; the odour may be completely removed by keeping the product for some time over oil of vitriol.

*Properties.* Crystallises from solution in water, alcohol, or ether, in delicate shining anhydrous needles. — Impure bipyrotartramide, however, may remain liquid for a long time at the ordinary temperature of a room, if it contains but a trace of water, a peculiarity perhaps arising from the presence of an empyreumatic oil; but even in that case it soon solidifies when immersed in snow. — [Biffi obtained the compound in small white laminæ which melted at the heat of the water-bath. (*Ann. Pharm.* 91, 105).] The compound has a cooling, slightly bitter and sour taste. Melts at 66° to an oil which, on cooling, solidifies in a laminated crystalline mass, greasy to the touch. Volatilises at 100°, but does not begin to boil till heated above 280°. The boiling point is not constant. The aqueous solution has an acid reaction.

| | | | Arppe. | Biffi. |
|---|---|---|---|---|
| 10 C | 60 | 53·10 | 52·93 | 53·1 |
| N | 14 | 12·39 | 12·60 | |
| 7 H | 7 | 6·19 | 6·17 | 6·5 |
| 4 O | 32 | 28·32 | 28·30 | |
| $C^{10}NH^7O^4$ | 113 | 100·00 | 100·00 | |

*Decomposition.* Bipyrotartramide boiled with a large excess of strong solution of potash, gives off ammonia and forms pyrotartrate of potash.

*Combinations.* — Dissolves in *water;* readily in the ordinary *acids* and *alkalis;* does not combine with ammonia.

*Lead-compound.* — Lead-oxide dissolves abundantly in an aqueous solution of bipyrotartramide, and the alkaline solution dries up to an amorphous mass, containing 5·47 p. c. (5 At.) water, which go off at 100°, and not completely redissolved by water.

| *Dried over oil of vitriol.* | | | Arppe. |
|---|---|---|---|
| 2 $C^{10}NH^7O^4$ | 226 | 27·20 | 27·30 |
| 5 PbO | 560 | 67·39 | 67·23 |
| 5 HO | 45 | 5·41 | 5·47 |
| $C^{10}NH^7O^4,5PbO + 5Aq$ | 831 | 100·00 | 100·00 |

Bipyrotartramide does not combine with oxide of silver.

Bipyrotartramide is soluble in *alcohol* and in *ether*. (Arppe.) ¶.

*Chlorine-nucleus* $C^{10}Cl^3H^7$.

## Terchlorovalerianic Acid.

$C^{10}Cl^3H^7O^4 = C^{10}Cl^3H^7,O^4$.

DUMAS & STAS. (1840.) *Ann. Chim. Phys.* 73, 136; also *Ann. Pharm.* 35, 149; also *J. pr. Chem.* 21, 283.

*Trichlorbaldriansäure, Acide chlorovalerisique.*

*Preparation.* Dry chlorine gas is passed in the dark through dry valerianic acid, the liquid being at first cooled with cold water, that it may not be thrown about, but afterwards, when it begins to assume a more viscid consistency, heated to 50° or 60°; the passage of the chlorine is continued as long as hydrochloric acid is evolved, and afterwards carbonic acid gas passed through the liquid as long as it drives out chlorine and hydrochloric acid.

*Properties.* — Colourless, transparent oil, very thick at — 18°, semi-fluid at ordinary temperatures, very mobile at 30°. Heavier than water. Inodorous; tastes sharp and burning, and makes a white spot upon the tongue.

| | | | Dumas & Stas. |
|---|---|---|---|
| 10 C | 60·0 | 29·24 | 29·60 |
| 3 Cl | 106·2 | 51·76 | 50·80 |
| 7 H | 7·0 | 3·41 | 3·45 |
| 4 O | 32·0 | 15·59 | 16·15 |
| $C^{10}Cl^3H^7O^4$ | 205·2 | 100·00 | 100·00 |

*Decomposition.* — The acid gives off a large quantity of hydrochloric acid between 110° and 120°.

*Combinations.* The acid takes up water immediately, and forms a very fluid hydrate, which sinks in water, and does not give off the whole of its water even at 100° in vacuo.

From its solution in [concentrated?] alkalis, it is precipitated by stronger acids.

The recently-prepared dilute aqueous solution does not precipitate nitrate of silver; but the hydrate forms with it a copious precipitate, perfectly soluble in nitric acid. (Dumas & Stas.)

*Chlorine-nucleus* $C^{10}Cl^4O^6$.

## Quadrichlorovalerianic Acid.

$C^{10}Cl^4H^6O^4 = C^{10}Cl^4H^6,O^4$.

DUMAS & STAS. (1840.) *Ann. Chim. Phys.* 73, 139; also *Ann. Pharm.* 35, 150; also *J. pr. chem.* 21, 285.

*Quadrichlorbaldriansäure, Acide chlorovalerosique.*

*Preparation.* Dry chlorine gas is passed in sunshine, through dry valerianic acid, at first in the cold, afterwards at 60°, till the formation of

hydrochloric acid ceases, and afterwards carbonic acid gas passed through the liquid for several hours to expel the free chlorine and hydrochloric acid which colour the acid yellow.

*Properties.* Colourless, semi-fluid oil, which does not soldify at —15°; heavier than water; not volatile; inodorous; and having a burning, somewhat bitter taste.

| | | | Dumas & Stas. |
|---|---|---|---|
| 10 C | 60·0 | 25·04 | 24·97 |
| 4 Cl | 141·6 | 59·10 | 59·10 |
| 6 H | 6·0 | 2·50 | 2·59 |
| 4 O | 32·0 | 13·36 | 13·34 |
| $C^{10}Cl^4H^6O^4$ | 239·6 | 100·00 | 100·00 |

*Decompositions.* 1. In the dry state, the acid remains unaltered at ordinary temperatures and at 150°, but decomposes at higher temperatures, with evolution of hydrochloric acid. — 2. It is not decomposed by ammonia, but quickly by excess of potash or soda, with formation of a chloride and a brown substance.

*Combinations.* The acid shaken up with a small quantity of *water* forms a thin oily hydrate and above it an aqueous solution. — *a.* The hydrate becomes turbid at — 18°, with separation of ice. It decomposes with formation of hydrochloric acid, when heated, and even when merely left at rest for several days, so that it then precipitates nitrate of silver. It contains 23·3 p.c. C and 3·1 H, and is therefore $C^{10}Cl^4H^6O^4$, 2 HO.

*b.* In a large quantity of water, both the acid and its hydrate are abundantly soluble.

The *Quadrichlorovalerates* or *Chlorovalerosates* = $C^{10}Cl^4H^5MO^4$. The acid expels carbonic acid from the alkaline carbonates; its *ammonia*, *potash*, and *soda*-salts taste very sharp and bitter, and from these solutions [when not too dilute], stronger acids throw down the hydrate.

By precipitating nitrate of silver with the ammonia-salt, *quadrichlorovalerate of silver* is obtained as a white crystalline precipitate. This salt is gradually decomposed in the dark into white chloride of silver, and a substance which spots paper and is perhaps $C^{10}Cl^3H^6O^4$ [more probably: $C^{10}Cl^3H^5O^4$]. The silver-salt dissolves sparingly in water, readily in nitric acid; and these solutions, when exposed to light, deposit black chloride of silver.

| *Dried.* | | | Dumas & Stas. |
|---|---|---|---|
| 10 C | 60·0 | 17·31 | 17·0 |
| 4 Cl | 141·6 | 40·86 | |
| 5 H | 5·0 | 1·44 | 1·5 |
| Ag | 108·0 | 31·16 | 31·6 |
| 4 O | 32·0 | 9·23 | |
| $C^{10}Cl^4H^5AgO^4$ | 346·6 | 100·00 | |

The acid dissolves readily in *alcohol* and *ether*; but the solutions, after a while, precipitate nitrate of silver. (Dumas & Stas.)

*Amidogen-nucleus* $C^{10}AdH^{9}$.

## Amylamine.

$C^{10}NH^{13} = C^{10}AdH^{9},H^{2}$. ?

WURTZ. (1849.) *Compt. rend.* 29, 186; also *N. J. Pharm.* 16, 277. — *N. Ann. Chim. Phys.* 30, 447.
BRAZIER & GOSSLETH. *Chem. Soc. Qu. J.* 3, 210; *Ann. Pharm.* 75, 252.

*Amyliaque, Valeramine, Ammoniaque valerique.*

*Formation.* 1. In the decomposition of cyanate of amyl (allophanate of amyl, — p. 74) cyanurate of amyl, or amyl-urea by potash :

$$C^{12}NH^{11}O^{2} + 2HO + 2KO = C^{10}NH^{13} + 2(KO,CO^{2});$$

and $$C^{12}N^{2}H^{14}O^{2} + 2HO + 2KO = C^{10}NH^{13} + 2(KO,CO^{2}) + NH^{3}.$$

¶. 2. By heating amylosulphate of lime with alcoholic ammonia :

$$C^{10}H^{11}Ca,2SO^{4} + NH^{3} = C^{10}NH^{13},HSO^{4} + CaSO^{4}.$$

The mixture heated to 250° for two hours in a sealed tube, yields a mass, which when distilled with potash, gives off amylamine. Amylosulphate of baryta appears to act in a similar manner. (Berthelot, *Compt. rend.* 36, 1098.) ¶.

*Preparation.* Cyanate of potash is distilled with amylosulphate of potash; the resulting distillate of cyanate and cyanurate of amyl again distilled with strong caustic potash, the cyanurate of amyl being decomposed after the water has passed over; the strongly alkaline distillate, which often consists of two layers, neutralized with hydrochloric acid, filtered, and evaporated on the water-bath; the hydrochlorate of amylamine which remains, purified by recrystallisation and distilled with lime; and the amylamine which passes over, rectified by distillation over baryta or hydrate of potash. (Wurtz.) Since crude cyanide of amyl (p. 67) when prepared from cyanide of potassium containing cyanate of potash, is contaminated with allophanate of amyl, it follows that when such impure cyanide is boiled with alcoholic potash to obtain caproate of potash, the alcohol and fusel-oil which pass over are accompanied by amylamine; and consequently, when the distillate, after being mixed with hydrochloric acid, is evaporated to a syrup, this syrup diluted with water, whereupon an additional portion of fusel-oil separates out, and the liquid separated therefrom boiled for a while to expel the rest of the fusel-oil, a liquid is obtained, which, when subsequently distilled with potash, yields pure amylamine. (Brazier & Gossleth.)

*Properties.* Colourless, very thin liquid, of sp. gr. 0·7503 at 18°, boiling at 95°, smelling of ammonia and fusel-oil, and having a burning, caustic and bitter taste. (Wurtz.) Boils at 93°. (Brazier & Gossleth.)

| | | | Wurtz. |
|---|---|---|---|
| 10 C | 60 | 68·97 | 68·52 |
| N | 14 | 16·09 | |
| 13 H | 13 | 14·94 | 15·03 |
| $C^{10}NH^{13}$ | 87 | 100·00 | |

*Decompositions.* 1. Amylamine burns with a bright flame. (Wurtz.)— 2. With bromine it forms hydrobromate of amylamine and insoluble drops of a bromine-compound. (Wurtz.) — 3. Supersaturated with hydrochloric acid and gradually dropt into a warm aqueous solution of nitrate of potash, it gives off a large quantity of nitrogen and yields an oily distillate of nitrite of amyl.

$$C^{10}NH^{13} + 2NO^{3} = C^{10}NH^{11}O^{4} + 2HO + 2N. \quad \text{(Wurtz.)}$$

At the same time, however, there are formed a few easily fusible laminæ having a fatty lustre, which partly distil over with the amylic nitrite and afterwards separate from it, partly remain behind with the chloride of potassium. (Hofmann, *Ann Pharm.* 75, 364.)

*Combinations.* Amylamine mixes in all proportions with *water.*

*Salts of Amylamine.*— The following bases are precipitated from their solutions in acid by amylamine: Magnesia, alumina, the sesquioxides of chromium and uranium, protoxide of manganese, the teroxides of antimony and bismuth, oxide of zinc, oxide of cadmium, protoxide of tin, protoxide of lead (from nitric but not from acetic acid), sesquioxide of iron, the protoxides of cobalt, nickel and copper, mercurous oxide, corrosive sublimate (white precipitate), oxide of silver, and teroxide of gold; an excess of it redissolves alumina, oxide of copper, oxide of silver, and oxide of gold. (Wurtz.)

*Carbonate of Amylamine.*— Formed as a crystalline deposit on the sides of vessels containing amylamine and exposed to the air.

*Sulphate of Amylamine.* — Formed by heating amylosulphate of lime or baryta with alcoholic ammonia. (Berthelot, p. 58.)

*Hydrobromate of Amylamine.*— Melts at a strong heat and diffuses white inflammable vapours. Permanent in the air, very soluble in water and alcohol, very sparingly in ether, which precipitates it from concentrated alcoholic solutions. (Wurtz.)

| | *Crystals.* | | Wurtz. |
|---|---|---|---|
| 10 C | 60·0 | 48·62 | 48·2 |
| N | 14·0 | 11·35 | |
| 14 H | 14·0 | 11·35 | 11·4 |
| Cl | 35·4 | 28·68 | 28·3 |
| $C^{10}NH^{13},HCl$ | 123·4 | 100·00 | |

Amylamine in excess redissolves *alumina* precipitated from its salts by a smaller quantity of amylamine (a property which may be made available for the separation of alumina from sesquioxide of iron); also *cupric oxide* with azure colour, but not so readily as ammonia; also, but

without colour and only when in great excess, the tawny resinous precipitate which a smaller quantity of amylamine produces in *nitrate of silver;* and the yellow-brown gummy precipitate which it forms in *solution of gold.* It also dissolves chloride of silver, but not so readily as ammonia. (Wurtz.)

*Platinum-salt.* — Hydrochlorate of amylamine and bichloride of platinum, mixed in concentrated aqueous solutions, with addition of a little alcohol, yield a precipitate, which, after being collected on a filter and pressed, separates from solution in boiling water in golden yellow scales. (Wurtz.)

| | | | Wurtz. | Brazier & Gossleth. |
|---|---|---|---|---|
| 10 C | 60·0 | 20·46 | 20·47 | 20·30 |
| N | 14·0 | 4·78 | | |
| 14 H | 14·0 | 4·78 | 4·85 | 5·00 |
| Pt | 99·0 | 33·76 | 32·60 | 33·45 |
| 3 Cl | 106·2 | 36·22 | 35·88 | |
| $C^{10}NH^{13},HCl + PtCl^2$ | 293·2 | 100·00 | | |

*Amyloxamide.*— Amylamine in contact with oxalate of ethyl becomes strongly heated, and solidifies in silky needles. These crystals melt at 139°; volatilize without residue at a stronger heat, diffusing white vapours; are insoluble in water; but dissolve in boiling alcohol, from which they separate almost completely on cooling. (Wurtz). [The mode of formation is probably as follows]:

$$C^{12}H^{10}O^8 + 2(C^{10}NH^{13}) = C^{24}N^2H^{24}O^4 + 2(C^4H^6O^2.)$$

## ¶. Biamylamine.

$$C^{20}NH^{23} = C^{10}Ad(C^{10}H^{11})H^8,H^2. ?$$

A. W. Hofmann. *Phil. Trans.* 1851, II, 357; *Ann. Pharm.* 79, 20; *Chem. Soc. Qu. J.* 4, 322.

*Diamylaminé.* — May also be regarded as $(C^{10}H^{10})^2,H^3N$, or as $(C^{10}H^{11})^2H,N$.

Formed as a hydrobromate by the action of bromide of amyl on amylamine. The action takes place slowly in the cold, rapidly at 100°. The resulting white crystalline mass decomposed by potash yields the base.

Biamylamine when pure is a light oily liquid, which boils at about 170°, has a peculiar though not unpleasant odour, like that of amylamine, and a hot pungent taste. It is but very sparingly soluble in water, to which however it imparts an alkaline reaction.

Biamylamine combines with acids, forming salts which dissolve but sparingly in cold water, but may be recrystallised from boiling water. The *Hydrochlorate* is nearly insoluble in cold water; its warm solution forms with bichloride of platinum a beautiful *Platinum-salt,* which dissolves

pretty easily in water, and often separates from the solution in oily drops which gradually solidify in the crystalline form.

| *Hydrochlorate.* | | | Hofmann. |
|---|---|---|---|
| $C^{20}NH^{23}$ | 157·0 | 81·19 | |
| HCl | 36·4 | 18·81 | 18·51 |
| $C^{20}NH^{23},HCl$ | 193·4 | 100·00 | |

| *Platinum-salt.* | | | Hofmann. |
|---|---|---|---|
| $C^{20}NH^{23}$ | 193·4 | 53·26 | |
| 2 Cl | 70·8 | 19·49 | |
| Pt | 99·0 | 27·25 | 27·10 |
| $C^{20}NH^{23},HCl,PtCl^2$ | 363·2 | 100·00 | |

## ¶. Metethamylamine.

$$C^{16}NH^{19} = C^{10}Ad(C^2H^3)(C^4H^5)H^7,H^2. ?$$

A. W. HOFMANN. *Ann. Pharm.* 78, 285; *Chem. Soc. Qu. J.* 4,317.

*Methylethylamylamine, Formovinamylamine.* — May be regarded as $(C^2H^2)(C^4H^4)(C^{10}H^{10}),NH^3$, or as $(C^2H^3)(C^4H^5)(C^{10}H^{11})N$.

Obtained by the dry distillation of hydrate of methylobiethamylamine (p. 110), water and olefiant gas being given off at the same time :

$$C^{20}NH^{23},2HO = C^{16}NH^{19} + 2HO + C^4H^4.$$

Transparent oil, having a fragrant odour and similar taste. Dissolves sparingly in water, to which it imparts an alkaline reaction. After being dried over hydrate of potash and rectified, it boils constantly at 135°.

Dissolves slowly in acids. The hydrochlorate forms with bichloride of platinum, a double salt which is very soluble in water, and is usually precipitated on mixing the two salts in strong solution, or on evaporating the mixture, in deep orange-yellow oily globules, which gradually solidify in magnificent needles.

| *Platinum-salt.* | | | Hofmann. |
|---|---|---|---|
| $C^{16}NH^{19}$ | 165·4 | 49·35 | |
| 2 Cl | 70·8 | 21·13 | |
| Pt | 99·0 | 29·52 | 29·36 |
| $C^{16}NH^{19},HCl,PtCl^2$ | 335·2 | 100·00 | |

## ¶. Biethamylamine.

$$C^{18}NH^{21} = C^{10}Ad(C^4H^5)^2H^7,H^2. ?$$

A. W. HOFMANN. *Ann. Pharm.* 78, 282; *Chem. Soc. Qu. J.* 4, 315.

*Diethamylamine, Bivinamylamine.*—May also be regarded as $(C^4H^4)^2(C^{10}H^{10}),NH^3$, or as $(C^4H^5)^2(C^{10}H^{11})N$.

Obtained, together with water and olefiant gas, by the dry distillation of hydrate of triethamylamine (p. 111).— Oily liquid, heavier than water, having a not unpleasant odour, and an analogous, somewhat bitter taste. After drying over hydrate of potash, it boils constantly at 154°, which is just 19° higher than the boiling point of metethamylamine (p. 108), agreeing therein with Kopp's law (vii, 55).

Biethamylamine is less soluble in water. and combines less readily with acids than metethamylamine. The *Sulphate, Hydrochlorate, Nitrate,* and *Oxalate* crystallise readily, but are deliquescent. The *Platinum-salt* separates on cooling from a concentrated mixture of the hydrochlorate with bichloride of platinum, in orange-yellow needles of extraordinary beauty.

| *Platinum-salt.* | | | Hofmann. |
|---|---|---|---|
| $C^{18}NH^{21},HCl$ | 179·4 | 51·37 | |
| 2 Cl | 70·8 | 20·27 | |
| Pt | 99·0 | 28·36 | 28·03 |
| $C^{18}NH^{21},HCl,PtCl^2$ | 349·2 | 100·00 | |

## ¶. Triamylamine.

$$C^{30}NH^{33} = C^{10}Ad(C^{10}H^{11})^2H^7,H^2. \ ?$$

A. W. Hofmann. *Ann. Pharm.* 79, 22; *Chem. Soc. Qu. J.* 4, 323.

May also be regarded as $(C^{10}H^{10})^3NH^3$, or as $(C^{10}H^{11})^3N$.

Obtained: 1. By the action of bromide of amyl on biamylamine.— 2. By dry distillation of hydrate of tetramylamine (p. 111.) Resembles biamylamine in most of its properties. Boils at 257°.

The *Hydrochlorate* separates immediately as a nacreous crystalline mass, on mixing the base with strong hydrochloric acid; and on adding bichloride of platinum to the solution, the *Platinum-salt* separates as a viscid mass, which gradually solidifies in the crystalline form.

| *Hydrochlorate.* | | | Hofmann. |
|---|---|---|---|
| $C^{30}NH^{33}$ | 227·0 | 86·18 | |
| HCl | 36·4 | 13·82 | 13·73 |
| $C^{30}NH^{33},HCl$ | 263·4 | 100·00 | |

| *Platinum-salt.* | | | Hofmann. |
|---|---|---|---|
| $C^{30}NH^{33},HCl$ | 263·4 | 60·80 | |
| 2 Cl | 70·8 | 16·35 | |
| Pt | 99·0 | 22·85 | 22·82 |
| $C^{30}NH^{33},HCl,PtCl^2$ | 433·2 | 100·00 | |

## ¶. Methylobiethamylamine.

$$C^{20}NH^{23} = C^{10}Ad(C^2H^3)(C^4H^5)^2,H^6,H^2. ?$$ *

A. W. Hofmann. *Ann. Pharm.* 78, 283; *Chem. Soc. Qu. J.* 4, 316.

Supposing it to contain 1 At. H more, it may be regarded as *Methylobiethylamylammonium* = $C^2H^3,(C^4H^5)^2,C^{10}H^{11},N$.

Known only in combination with water and acids.

Obtained as a hydriodate by the action of iodide of methyl on biethamylamine.

$$[C^{18}NH^{21} + C^2H^3I = C^{20}NH^{23},HI \text{ or } C^{20}NH^{24},I.]$$

The methylic iodide must be added gradually; for on suddenly mixing, a violent action takes place and the liquid is projected with a kind of explosion: it is best also to make the mixture in a tubulated retort provided with a condenser. The mixture on cooling solidifies into a hard white crystalline mass of the hydriodate, This salt is very soluble in water, and forms a very bitter solution from which it is reprecipitated by potash in oily globules which solidify but slowly.

The hydriodate digested with oxide of silver, yields the *hydrate of methylobiethamylamine,* $C^{20}NH^{23},HO$ [or hydrated oxide of methylodiethylamylammonium: $(C^2H^3),(C^4H^5)^2,(C^{10}H^{11}),NO$] in the form of a strongly alkaline solution, which, when evaporated to dryness, and distilled, is resolved into water, olefiant gas and metethamylamine:

$$C^{20}NH^{23},HO = C^4H^4 + HO + C^{16}NH^{19}.$$

The hydrate forms crystalline salts with sulphuric, hydrochloric and nitric acid. The hydrochlorate mixed with bichloride of patinum forms a beautiful platinum-salt.

| | | | Hofmann. |
|---|---|---|---|
| $C^{20}NH^{23},HCl$ | 193·4 | 53·25 | |
| 2 Cl | 70·8 | 19·49 | |
| Pt | 99·0 | 27·26 | 27·29 |
| $C^{20}NH^{23},HCl,PtCl^2$ | 363·2 | 100·00 | |

or: $(C^2H^3)(C^4H^5)^2(C^{10}H^{11})N,Cl,PtCl^2$. (Hofmann.)

* This and the similar formulæ for the other amyl-bases containing 4 At. of the alcohol-radicals (pp. 111, 112) are given in accordance with those assigned by Gmelin to the corresponding bases of the phenyl-series (*q. v.*); but there can be little doubt that the formulæ originally given by Hofmann accord much more nearly with the observed chemical relations of these compounds.—[Tr.]

## ¶. Triethamylamine.

$C^{22}NH^{25} = C^{10}Ad(C^4H^5)^3H^6,H^2$. ?

A. W. Hofmann. *Ann. Pharm*, 78, 279; *Chem. Soc. Qu. J.* 313.

Supposing it to contain 1 At. H more, it may be regarded as *Triethylamylammonium* $= (C^4H^5)^3,C^{10}H^{11},N$.

Known only in combination with water and acids.

Obtained as a hydriodate by the action of iodide of amyl on triethylamine.

$$C^{12}NH^{15} + C^{10}H^{11}I = C^{22}NH^{25},HI.$$

The action is not very rapid, and to complete it, the mixture must be heated in a sealed tube for two or three days.

The solution of the hydriodate boiled with oxide of silver yields the *Hydrate* $C^{22}NH^{25}$, HO [or the oxide of triethylamylammonium $C^{22}NH^{26},O$] in the form of an alkaline solution having an extremely bitter taste. On evaporating this solution, the hydrate remains in the form of a syrup which does not show any disposition to crystallise. When distilled, it yields water, olefiant gas and biethamylamine:

$$C^{22}NH^{25},HO = HO + C^4H^4 + C^{16}NH^{19}.$$

The *Sulphate* and *Oxalate* of triethamylamine, when evaporated in vacuo, leave a syrupy or gummy residue like the base itself.

The *Hydriodate* forms very fine crystals, which exhibit the fatty lustre and touch peculiar to the amyl-compounds. It dissolves with great facility in water and alcohol, but is insoluble in ether. The solutions have the bitter taste of quinine. On the addition of potash or carbonate of potash, the hydriodate separates in the form of an oil, which rapidly shoots into brilliant needles. The salt when slightly moist, melts at 100° to a clear oily liquid, which becomes solid when cold and perfectly dry, and gradually turns yellow.

| | | | Hofmann. |
|---|---|---|---|
| $C^{22}NH^{25}$ | 171 | 57·39 | |
| HI | 127 | 42·61 | 42·66 |
| $C^{22}NH^{25},HI$ | 298 | 100·00 | |

The *Hydrochlorate* forms very deliquescent laminæ; the *Nitrate*, hard permanent needles having a cooling taste.

*Platinum-salt*. The solution of the hydrochlorate is not precipitated by bichloride of platinum, except when highly concentrated; but the salt when once formed, is much less soluble. From a boiling aqueous solution it shoots out in splendid orange-yellow needles, sometimes half an inch long.

| | | | Hofmann. |
|---|---|---|---|
| $C^{22}NH^{25},HCl$ | 207·4 | 54·98 | |
| 2 Cl | 70·8 | 18·77 | |
| Pt | 99·0 | 26·25 | 25·76 |
| $C^{22}NH^{25},HCl,PtCl^2$ | 377·2 | 100·00 | |

The deficiency in the platinum determination appears to be due to a peculiar decomposition which the platinum-salts of these bases undergo when their solutions are boiled; the salt in this instance had been recrystallised from boiling water. The decomposition in question cannot be discovered by any change of appearance, but only from the diminution in the amount of platinum. (Hofmann.)

## ¶. Tetramylamine.

$$C^{40}NH^{43} = C^{10}Ad(C^{10}H^{11})^3H^6,H^2. ?$$

A. W. Hofmann. *Ann. Pharm.* 79, 24; *Chem. Soc. Qu. J.* 4, 324.

Supposing it to contain 1 At. H more, it may be regarded as *Tetramylammonium* or *Tetramylium* = $(C^{10}H^{10})^4,NH^4$ or $(C^{10}H^{11})^4,N$.

Known only in combination with water or acids.

It is obtained as a hydriodate: 1. By the action of iodide of amyl on triamylamine, the mixture solidifying after three or four days' boiling into an unctuous crystalline mass. — 2. By heating iodide of amyl in a sealed tube with strong solution of ammonia. The action is however very slow, not being complete even after several weeks' boiling. The excess of iodide of amyl may be removed by distilling the liquid *per se*, and the ammonia and the lower amyl-bases by distillation with potash; the hydriodate of tetramylamine then remains in the form of a heavy oil which on cooling solidifies in a mass having the consistence of stearin. It dissolves sparingly in water, forming an extremely bitter liquid, from which it is re-precipitated in the crystalline form by alkalis. When dry it assumes a pale yellow colour.

| | | | Hofmann. |
|---|---|---|---|
| $C^{40}NH^{43}$ | 297 | 70·05 | |
| HI | 127 | 29·95 | 29·74 |
| $C^{40}NH^{43},HI$ | 424 | 100·00 | |

On boiling the hydriodate with oxide of silver, there is formed a very bitter alkaline solution of *hydrate of tetramylamine* [or oxide of tetramylium].

$$C^{40}NH^{43},HI + AgO = AgI + C^{40}NH^{43},HO.$$

This base is less soluble in water than the corresponding methyl and ethyl-compounds (vii, 320; ix, 66). On adding potash to the solution, the base rises to the surface in the form of an oily layer. The same effect takes place when the solution is strongly concentrated by evaporation; in the latter case, the oil gradually solidifies into a crystalline mass. A moderately concentrated solution of the base, left to evaporate in an atmosphere free from carbonic acid, deposits after a while, magnificent, perfectly definite crystals, sometimes an inch in length and thickness; they are but moderately deliquescent, and attract carbonic acid from the air but slowly. These crystals consist of the hydrate of tetramylamine with several atoms of water of crystallisation. When heated, they melt in their water of crystallisation, and on evaporation in the water-bath,

leave a semi-solid transparent mass consisting of the pure hydrate. This hydrate is decomposed, partially at the heat of the water-bath, completely at higher temperatures, into triamylamine, water, and a hydrocarbon, which is probably amylene :

$$C^{40}NH^{43},HO = C^{30}NH^{33} + HO + C^{10}H^{10}.$$

*Sulphate of Tetramylamine* crystallises in long, capillary threads; the *Nitrate* in needles; the *Oxalate* in large, well-developed plates, which are extremely bitter and deliquescent; the *Hydrochlorate* crystallises in leaves with palm-like ramifications. Its solution forms with chloride of *platinum* a pale yellow curdy precipitate which gradually solidifies in beautiful orange-yellow needles.

| | | | Hofmann. |
|---|---|---|---|
| $C^{40}NH^{43},HCl$ | 333·4 | 66·25 | |
| 2 Cl | 70·8 | 14·08 | |
| Pt | 99·0 | 19·67 | 19·63 |
| $C^{40}NH^{43},HCl,PtCl^2$ | 503·2 | 100·00 | |

or: $C^{40}NH^{44}Cl,PtCl = (C^{10}H^{11})^4N,Cl,PtCl^2$. (Hofmann.) ¶.

## Valeramide.

$$C^{10}NH^{11}O^2 = C^{10}AdH^9,O^2.$$

DUMAS, MALAGUTI & LEBLANC (1847). *Compt. rend.* 25, 475, and 658.

DESSAIGNES & CHAUTARD. *N. J. Pharm.* 13, 245; also *J. pr. Chem.* 45, 48.

*Formation and Preparation.* By placing valerate of ethyl in contact with aqueous ammonia. (Dumas, &c.)—1 vol. valerate of ethyl set aside with 8 vol. concentrated ammonia in a closed bottle and frequently shaken, requires four months in summer to disappear; and the liquid, if then evaporated at a gentle heat, leaves crystalline valeramide. (Dessaignes.)

Large, thin, shining laminæ which melt at 100°, and immediately afterwards sublime in very delicate, iridescent laminæ. Neutral. (Dessaignes & Chautard.)

| | | | Dessaignes & Chautard. |
|---|---|---|---|
| 10 C | 60 | 59·41 | 60·05 |
| N | 14 | 13·86 | |
| 11 H | 11 | 10·89 | 10·94 |
| 2 O | 16 | 15·84 | |
| $C^{10}NH^{11}O^2$ | 101 | 100·00 | |

*Decompositions.* 1. Valeramide heated with anhydrous phosphoric acid, is resolved into water and valeronitrile. (Dumas, &c.) So likewise when its vapour is passed over red-hot lime. (Hofmann.)

$$C^{10}NH^{11}O^2 = 2HO + C^{10}NH^9.$$

2. With potash-ley at the boiling heat, it gives off a small quantity of ammonia. (Dessaignes & Chautard.) — 3. Heated with potassium, it yields cyanide of potassium, hydrogen gas and a gaseous hydrocarbon. (Dumas, &c.)

*Combination.* — Valeramide dissolves very easily in water. (Dessaignes and Chautard.)

## Amylurethane.

$$C^{10}NH^{13}O^4 = C^{10}AdH^{11},2CO^2.$$

MEDLOCK. *Chem. Soc. Qu. J.* 2, 252; also *Ann. Pharm.* 71, 104.
WURTZ. *N. J. Pharm.* 17, 79.

*Carbonate of Amyl, Kohlenmylamester, Urethamylane.*

*Preparation.* Chloroformiate of amyl (p. 66), is mixed with aqueous ammonia, and the oil which rises to the surface and solidifies into a crystalline mass of amylurethane and sal-ammoniac, freed from fusel-oil by pressure between paper, and from sal-ammoniac by washing with water till the liquid which runs through no longer precipitates nitrate of silver. (Medlock.) — 2. The compound is also obtained by the action of chloride of cyanogen on fusel-oil. (Wurtz.)

$$C^{10}H^{12}O^2 + C^2NCl + 2HO = C^{12}NH^{13}O^4 + HCl.$$

*Properties.* Amylurethane separates on cooling from its solution in hot water, alcohol, or ether, in silky iridescent needles, which melt at 60°, distil over without change at 220°, and solidify in the neck of the retort into a crystalline mass having a fatty lustre. (Medlock.)

| | | | Medlock. | Wurtz. |
|---|---|---|---|---|
| 12 C | 72 | 54·96 | 55·11 | 54·81 |
| N | 14 | 10·69 | 10·70 | 10·71 |
| 12 H | 13 | 9·92 | 9·93 | 10·08 |
| 4 O | 32 | 24·43 | 24·26 | 24·40 |
| $C^{12}NH^{13}O^4$ | 131 | 100·00 | 100·00 | 100·00 |

*Decompositions.* The solution of amylurethane in oil of vitriol is resolved by heat into carbonic and sulphurous acid gases, sulphate of ammonia, and amylosulphuric acid. [According to the equation;

$$C^{12}NH^{13}O^4 + 4SO^3 + 2HO = C^{10}H^{12}O^2,2SO^3 + NH^3,2SO^3 + 2CO^2.$$

there should be no sulphurous acid produced; it is perhaps formed by further decomposition of the amylosulphuric acid by the excess of oil of vitriol]. — 2. When amylurethane is distilled with baryta, carbonate of baryta is formed, and ammonia and fusel-oil (but no valeramine) pass over. (Medlock.) The 2 HO required to form these products must be derived from another decomposition of a portion of the amylurethane. (Medlock.)

*Combinations.* — Amylurethane dissolves in boiling *water.*

It dissolves in cold *oil of vitriol,* and on addition of water rises to the surface unaltered, and forms a crystalline crust.

Dissolves in *alcohol* and *ether.* (Medlock.)

## Oxamylane.

$$C^{14}NH^{13}O^{6} = C^{10}AdH^{11},C^{4}O^{6}. ?$$

BALARD. (1844.) *Ann. Chim. Phys.* 12, 309; also *J. pr. Chem.* 34, 141.

Obtained by the action of dry ammoniacal gas on oxalate of amyl (p. 72).

Separates from its alcoholic solution in indistinct crystals.

Resolved by boiling with water, and more quickly with aqueous alkalis, into fusel-oil and oxamic acid (ix, 259). (Balard.)

## ¶. Sincaline.

$$C^{10}NH^{13}O^{2} = C^{10}AdH^{11},O^{2}.$$

BABO & HIRSCHBRUNN. *Ann. Pharm.* 84, 10.

*Formation.* By the action of alkalis on sinapine, the alkaloïd contained in white mustard:

$$\underbrace{C^{32}NH^{23}O^{10}}_{\text{sinapine.}} + 2HO = \underbrace{C^{10}NH^{13}O^{2}}_{\text{sincaline.}} + \underbrace{C^{22}H^{12}O^{10}.}_{\text{sinapic acid.}}$$

*Preparation.* Hydrosulphocyanate of sinapine is heated with baryta-water till the whole of the sinapic acid is extracted in the form of a baryta-salt; the filtrate acidulated with sulphuric acid and mixed with sulphate of copper and protosulphate of iron to precipitate the hydrosulphocyanic acid; an excess of baryta added to remove the sulphuric acid and the excess of iron and copper; the baryta removed by passing carbonic acid gas through the liquid; the carbonate of sincaline, which then remains in solution, converted into a hydrochlorate; this salt decomposed by digestion with oxide of silver; and the filtrate evaporated over the water-bath or in vacuo.

*Properties.* Crystalline mass, colourless or slightly brown.

*Decomposition.* Sincaline cannot be volatilised without alteration; when distilled, it gives off combustible vapours having the odour of methylamine, and leaves a carbonaceous residue.

*Combinations.* Sincaline dissolves in *water;* when exposed to the air it becomes heated, deliquesces, and is converted into a *carbonate.*

It dissolves *sulphur;* and on adding a mineral acid to the solution, it gives off sulphuretted hydrogen, and deposits sulphur, which renders the liquid milky.

Sincaline precipitates most metallic oxides from their solutions, not excepting lime, baryta, and mercuric oxide. The precipitates which it forms in salts of alumina and of chromic oxide, redissolve in excess, and the chromic oxide is reprecipitated on boiling the solution.

*Gold-salt.* — Precipitated on mixing hydrochlorate of sincaline with terchloride of gold, in the form of a yellow crystalline powder, which is but sparingly soluble in cold water. It dissolves in boiling water, and crystallises on cooling, in the form of needles grouped in tufts.

| | *Dried at* 110°. | | | | Babo & Hirschbrunn. |
|---|---|---|---|---|---|
| 10 C | 60·0 | .... | 13·49 | ........ | 13·63 |
| N | 14·0 | .... | 3·15 | | |
| 14 H | 14·0 | .... | 3·15 | ........ | 3·38 |
| Au | 199·0 | .... | 44·77 | ........ | 44·54 |
| 4 Cl | 141·6 | .... | 31·85 | | |
| 2 O | 16·0 | .... | 3·59 | | |
| $C^{10}NH^{13}O^2,HCl,AuCl^3$ | 444·6 | .... | 100·00 | | |

*Platinum-salt.* — Obtained in splendid orange-coloured prisms or six-sided tables, by evaporating a mixture of hydrochlorate of sincaline and bichloride of platinum.

| | *Dried at* 110°. | | | | Babo & Hirschbrunn. |
|---|---|---|---|---|---|
| 10 C | 60·0 | .... | 19·39 | ........ | 19·65 |
| N | 14·0 | .... | 4·52 | | |
| 14 H | 14·0 | .... | 4·52 | ........ | 5·13 |
| Pt | 99·0 | .... | 32·00 | ........ | 31·36 |
| 3 Cl | 106·4 | .... | 34·40 | | |
| 2 O | 16·0 | .... | 5·17 | | |
| $C^{10}NH^{13}O^2,HCl,PtCl^2$ | 309·4 | .... | 100·00 | | |

Babo & Hirschbrunn suppose sincaline to contain 1 At. H more than is here assigned to it, making the formula $C^{10}NH^{14}O^2$; this agrees rather better with the analysis of the gold and platinum-salts, making the hydrogen in the former 3·36 p.c., and in the latter 4·83 ; but it is improbable, because it gives an uneven number for the sum of the numbers of atoms of N and H. (*vid.* Gerhardt, *Traité de Chimie organique,* 2, 430.) ¶.

## ¶. Xanthamylamide.

$$C^{12}NH^{13}S^2O^2 = C^{10}AdH^{11},CS^2,CO^2.$$

M. W. Johnson. *Chem. Soc. Qu. J.* 5, 142; abstr. *Ann. Pharm.,* 84, 336; *N. Ann. Chim. Phys.* 36, 361; *Jahresber.* 1852, 605.

Produced, together with amyloxanthate of ammonia, by the action of ammonia on bioxysulphocarbonate of amyl (p. 62).

$$2C^{12}H^{11}S^4O^2 + 2NH^3 = C^{12}NH^{13}S^2O^2 + C^{10}H^{11}(NH^4,)O^2,2CS^2 + 2S.$$

The bioxysulphocarbonate of amyl is digested at a gentle heat with strong aqueous ammonia, whereupon sulphur quickly separates out, and a yellow liquid is produced with oily particles suspended in it; and the solution of amyloxanthate of ammonia thus formed is passed through a wet filter, which retains the oily liquid together with the sulphur. The oily liquid, which is the xanthamylamide, is then washed with water, and separated from the sulphur by means of a dry filter, and dried, first in vacuo over sulphuric acid, afterwards more completely by passing a stream of dry carbonic acid gas through it at a gentle heat.

The process which was adopted with advantage by Debus in the preparation of xanthamide (ix, 276), viz., passing dry ammoniacal gas into the alcoholic solution of the bioxysulphocarbonate, evaporating, and treating the residue with ether to separate the amide from the ammonia-salt formed at the time, was found not to be applicable to the case of amyl-compound, because the amide and the amyloxanthate of ammonia are nearly equally soluble in ether.

*Properties.* — Yellow oily liquid neutral to test-paper. Boils at 184°, but not without decomposition.

| | | | Johnson. |
|---|---|---|---|
| 12 C | 72 | 48·98 | 49·24 |
| N | 14 | 9·52 | |
| 13 H | 13 | 8·85 | 10·04 |
| 2 S | 32 | 21·77 | 20·91 |
| 2 O | 16 | 10·88 | |
| $C^{12}NH^{13}S^2O^2$ | 147 | 100·00 | |

The analytical numbers are only approximative, because the compound could not be purified by distillation.

*Decompositions.* 1. Xanthamylamide is resolved by distillation into amylic mercaptan and cyanuric acid:

$$3C^{12}NH^{13}S^2O^2 = 3C^{10}H^{12}S^2 + C^6N^3H^3O^6.$$

When heated on platinum-foil, it gives off white vapours and burns with a yellow luminous flame.— 2. When boiled with hydrate of baryta, it is resolved into amylic alcohol and sulphocyanide of barium, ammonia being however evolved at the same time:

$$C^{12}NH^{13}S^2O^2 + BaO,HO = C^{10}H^{12}O^2 + C^2NBaS^2 + 2HO.$$

[This equation does not account for the evolution of ammonia; did it arise from an impurity?] Potash exerts a similar reaction.—3. *Chlorine-water* decomposes the compound, with separation of sulphur and formation of volatile oil. Hydrochloric acid has no action upon it, even at a boiling heat.— 4. Fuming *nitric acid* acts violently upon it, giving off red vapours, and water added to the solution causes the separation of oily drops.

*Combinations.* — Xanthamylamide is insoluble in water.

It dissolves in cold *oil of vitriol*, and water added to the solution separates oily drops.

*Iodine* dissolves in cold xanthamylamide, forming a red solution, which when heated, is decolorised, with separation of a colourless oil. — *Bromine*

forms with xanthamylamide a white solid mass which yields a milky liquid with alcohol; and on adding water to this liquid, a colourless oil separates out.

An alcoholic solution of xanthamylamide does not precipitate an alcoholic solution of acetate of lead or protochloride of copper.

*Mercury-compound.* — Xanthamylamide and mercuric chloride, both dissolved in alcohol, form a copious precipitate consisting of white feathery crystals, which may be purified by washing with cold alcohol, and dissolving in a large quantity of boiling alcohol; the solution on cooling deposits the mercury-compound in the pure state.

| *Dried in vacuo.* | | | Johnson. |
|---|---|---|---|
| 12 C | 72·0 | 10·46 | 10·60 |
| N | 14·0 | 2·03 | 1·48 |
| 13 H | 13·0 | 1·89 | 2·06 |
| 4 Hg | 400·0 | 58·09 | 58·06 |
| 4 Cl | 141·6 | 20·56 | |
| 2 S | 32·0 | 4·65 | |
| 2 O | 16·0 | 2·32 | |
| $C^{12}NH^{13}S^2O^2,4HgCl$ | 688·6 | 100·00 | |

This compound is insoluble in water, but is gradually decomposed by prolonged contact with water, an odour of fusel-oil becoming perceptible. Cold oil of vitriol immediately decomposes it, with rise of temperature, blackening, and evolution of hydrochloric acid. — Nitric acid acts with energy upon it. — Cold hydrochloric acid has no effect upon it; but on boiling, a portion of the mercuric chloride is dissolved out, and another compound formed containing a smaller amount of the mercuric chloride: this latter compound is a soft, white solid substance, which adheres with tenacity to the sides of the vessels, and when heated, melts into a white opaque oil. — Concentrated ammonia, in the cold, immediately decomposes the original mercury compound, with formation of black mercuric sulphide. — The compound boiled with potash forms a black precipitate and emits an odour of fusel-oil. Baryta likewise decomposes it at a boiling heat, an aromatic volatile compound being evolved, and mercuric sulphide remaining behind. — Sulphuretted hydrogen decomposes the compound, separating an oily liquid, which is doubtless xanthamylamide, but obstinately retains the hydrochloric acid generated in the reaction.

An alcoholic solution of xanthamylamide does not precipitate an alcoholic solution of nitrate of *silver.*

An aqueous solution of *bichloride of platinum* forms with an alcoholic solution of xanthamylamide, a copious yellow precipitate having a faint peculiar odour, and slightly soluble in alcohol; the solution when evaporated, deposits a yellow crystalline compound, the mother-liquor quickly turning brown, and on evaporation, deposits an amorphous brown residue, with copious evolution of hydrochloric acid. An alcoholic solution of biochloride of platinum forms no precipitate with xanthamylamide, but the solution on evaporation deposits a red crystalline compound.

Xanthamylamide dissolves readily in *alcohol* and *ether.* (Johnson.) ¶.

*Amidogen-nucleus* $C^{10}Ad^2H^2O^6$.

## Inosinic Acid.

$C^{10}N^2H^6O^{10} = C^{10}Ad^2H^2O^6,O^4$. ?

LIEBIG. *Ann. Pharm.* 62, 317.

From τοῦ ἰνός muscle. — Occurs in many kinds of muscular flesh. (Liebig.) The flesh of poultry yields 0·11 p.c. of inosate of baryta ; but the heart of the ox and the flesh of the ox, pigeon, ray and cod does not yield any. (Gregory, *Ann. Pharm.* 64, 106); neither does human flesh. (Schlossberger, *Ann. Pharm.* 66, 80.)

*Preparation.* — Flesh-juice is neutralised with baryta-water, and evaporated in a strong current of air at 60° (because inosinic acid is decomposed at 100°), till all the creatine has separated out (x, 250, *b*); the mother-liquor then evaporated somewhat further; gradually mixed with small portions of alcohol till it becomes milky; then set aside for a few days; and the resulting white or yellow, granular, laminar or needle-shaped crystals (a mixture of inosate of baryta, and creatine, together with phosphate of lime, if only a small quantity of baryta-water has been added, or inosate of potash, if the baryta-water has been added in excess), collected on a filter, and washed with alcohol; and its solution in hot water mixed with chloride of barium, whereupon it yields on cooling crystals of inosate of baryta, which are purified by recrystallisation. To obtain the free acid, either the solution of the baryta-salt is decomposed by the exact quantity of sulphuric acid required;—or the copper-salt is prepared by decomposing the baryta-salt with acetate of copper, then suspended in water, and decomposed by sulphuretted hydrogen; the filtrate, which exhibits a brown turbidity from the presence of sulphide of copper, decolorised with animal charcoal, and the filtrate evaporated to a syrup.

*Properties.* — The syrup obtained by evaporation does not yield any crystals, even after standing for a week, but when covered with alcohol, it is converted into a powder. It has an agreeable taste like that of broth and reddens litmus strongly.

*Decompositions.* — 1. The syrupy acid, evaporated with nitric acid, yields a small quantity of colourless crystalline grains. — 2. Heated with peroxide of lead and dilute sulphuric acid, it turns the peroxide white and forms a liquid, which, after removal of the sulphuric acid, yields needles by evaporation.

*Combinations.* — Inosinic acid dissolves readily in *water*, and is precipitated from the concentrated solution by alcohol in white amorphous flakes.

The *Inosates of the Alkalis*, when heated on platinum-foil, give off a strong but pleasant odour, like that of roast meat.

*Inosate of Potash.* — Obtained in part directly from the flesh-juice (*vid. sup.*), partly by careful precipitation of the baryta-salt with carbonate

of potash.—Long, slender, four-sided prisms which give off 22·02 p.c. water at 100°, and in the dry state contain 20·73 p. c. potash. They dissolve readily in water, but are insoluble in alcohol, and are precipitated by alcohol from the dilute aqueous solution, in the form of a white granular powder, but from the concentrated solution, in delicate nacreous laminæ which thicken the liquid to a pulp.

*Inosate of Soda.* — Fine silky needles, very easily soluble in water, insoluble in alcohol.

*Inosate of Baryta.* — The free acid does not precipitate baryta-water, but when the liquid is set aside and evaporated, laminæ of the salt are produced. (*Preparation, p.* 119).—Nacreous, elongated, four-sided laminæ, which after drying look like polished silver. They give off 19·07 p.c. water ( = 7 [6] At.) at 100°. Dissolve in 400 pts. water at 15°, more readily in hot water, but less in water at 100° than at 70°. The solution saturated at 70° deposits part of the salt on boiling in the form of a resinous mass. If a quantity of the salt, which would dissolve in a certain quantity of water at 60° to 70°, is heated with the same quantity of water to the boiling point, a portion of the salt remains undissolved, and by continued boiling, even loses its solubility in water of a lower temperature.

| *At* 100°. | | | Liebig. |
|---|---|---|---|
| BaO | 76·6 | 31·71 | 30·41 |
| 10 C | 60·0 | 24·83 | 24·63 |
| 2 N | 28·0 | 11·59 | 11·37 |
| 5 H | 5·0 | 2·07 | 2·61 |
| 9 O | 72·0 | 29·89 | 30·98 |
| $C^{10}N^2H^5BaO^{10}$ | 241·6 | 100·00 | 100·00 |

| *Crystals.* | | | Liebig. |
|---|---|---|---|
| $C^{10}N^2H^5BaO^{10}$ | 241·6 | 81·73 | 80·93 |
| 6 HO | 54·0 | 18·27 | 19·07 |
| $C^{10}N^2H^5BaO^{10} + 6Aq$ | 295·6 | 100·00 | 100·00 |

Liebig gives for the salt dried at 100°, the formula $BaO,C^2N^2H^6O^{10}$.

With *lime*-water, free inosinic acid behaves as with baryta-water.
It gives a white precipitate with *lead*-salts.

*Inosate of Copper.*— The free acid and its soluble salts form with acetate of copper, a beautiful green-blue precipitate, which dries up to a light blue amorphous powder, and does not blacken when boiled with water, or dissolve, with the exception of a mere trace; it is insoluble in acetic acid, but dissolves with blue colour in ammonia.

*Inosate of Silver.*— The alkaline inosates form with nitrate of silver a white gelatinous precipitate resembling alumina, which scarcely blackens on exposure to light, and dissolves to a small extent in pure water, less in silver-solution, and abundantly in nitric acid or ammonia. 100 pts. of the dry potash-salt form with silver-solution, a precipitate containing 49·99 p. c. oxide of silver.

*Alcohol* dissolves oily traces of inosinic acid; *ether* none. (Liebig.)

*Azo-nucleus* $C^{10}NH^9$.

## Valeronitrile.

$C^{10}NH^9$.

SCHLIEPER. (1846.) *Ann. Pharm.* 59, 15.
DUMAS, MALAGUTI & LEBLANC. *Compt. rend.* 25, 658.
GUCKELBERGER. *Ann. Pharm.* 64, 72.

*Cyanide of Butyl, Cyanhydrate de Butyrène.*

*Formation and Preparation.* 1. Dry valerate of ammonia or valeramide is distilled with anhydrous phosphoric acid. (Dumas, &c.)

$$NH^3,C^{10}H^{10}O^4 = C^{10}NH^9 + 4HO$$

and:

$$C^{10}NH^{11}O^2 = C^{10}NH^9 + 2HO.$$

Valeronitrile may also be produced, but not so readily, by passing valeramide through a red-hot tube filled with lime. (A. W. Hofmann, *Ann. Pharm.* 65, 56.)

2. When glue (Schlieper) or casein (Guckelberger) is distilled with chromate of potash and dilute sulphuric acid, valeronitrile passes over together with several other products. — 2 pts. of glue are left to swell up in 50 pts. of water; 15 pts. of oil of vitriol added; and the mixture, after cooling, poured into a retort containing 8 pts. of bichromate of potash and distilled, till, towards the end, the liquid, which becomes continually greener, no longer boils quietly, but begins to froth strongly. The distillate thus obtained, which is white and turbid, has an acid reaction, and smells strongly of hydrocyanic acid, is rectified over mercuric oxide, which decomposes the formic acid present, with evolution of gas, and retains the hydrocyanic acid, in the form of cyanide of mercury; and the liquid which first passes over, mixed with oily drops, is collected apart and several times fractionally rectified *per se*, till the oil which passes over is accompanied by 'only a small quantity of watery liquid, — then at a gentle heat over magnesia, to retain the benzoic acid, the receiver being changed as soon as, in place of a transparent, colourless oil and a clear watery liquid, a milky liquid gradually depositing oily drops, begins to pass over. The first oil is dehydrated by means of chloride of calcium, and slowly distilled with the thermometer; the receiver changed at 110°, because that which passes over at 90° is chiefly valeracetonitrile, while at 110°, the mixture of that body with valetronitile, and from 110° to 140° principally the latter distils over; and this last distillate subjected to two more distillations, the portion which distils over between 122° and 130° being collected apart in the former, and that which passes over between 124° and 127° in the latter: this last portion is pure valeronitrile. (Schlieper). — Or 1 pt. of casein is dissolved in a mixture of 3 pts. oil of vitriol and 6 pts. water contained in a retort; a solution of 2 pts. bichromate of potash in 10 pts. water added (a larger quantity would produce valerianic acid instead of valeronitrile); the reaction

which ensues moderated by the addition of 14 pts. more water (30 pts. in all); the distillate shaken up and redistilled with mercuric oxide; the distillate thus obtained neutralized with chalk, and redistilled; and the neutral distillate subjected to repeated fractional rectification, whereby there is obtained, first a milky distillate mixed with drops of colourless oil, and ultimately the latter only. When this distillate is further rectified, propylic aldide passes over below 120°, and between 120° and 140°, chiefly valeronitrile, which may be purified by repeated rectification, the first and last portions that pass over being set aside. (Guckelberger.)

*Properties.* Transparent, colourless, very thin liquid which refracts light strongly, sp. gr. 0·81 (Schlieper); 0·813 at 15°. (Guckelberger.) Boils at 125° (Schlieper); at 125° to 128°. (Guckelberger.) — Vapour-density = 2·892. (Guckelberger.) Smells like bitter almond oil and salicylous acid (Schlieper), and has an aromatic, burning, and bitter taste. (Guckelberger.) Makes a transient grease-spot upon paper. (Schlieper.)

| | | | Schlieper. | Guckelberger. |
|---|---|---|---|---|
| 10 C | 60 | 72·29 | 71·93 | 71·86 |
| N | 14 | 16·87 | 16·95 | 16·79 |
| 9 H | 9 | 10·84 | 10·60 | 10·88 |
| $C^{10}NH^9$ | 83 | 100·00 | 99·48 | 99·53 |

| | Vol. | Density. |
|---|---|---|
| C-vapour | 10 | 4·1600 |
| N-gas | 1 | 0·9706 |
| H-gas | 9 | 0·6237 |
| Vapour of Valeronitrile | 2 | 5·7543 |
| | 1 | 2·8771 |

*Decompositions.* Valeronitrile, when set on fire, burns with a white luminous flame, and without smoke. (Schlieper, Guckelberger.) — 2. In sunshine, it is decomposed by chlorine or bromine, with formation of hydrochloric or hydrobromic acid. (Schlieper.) — 3. With oil of vitriol (also, according to Guckelberger, when distilled with dilute sulphuric acid), it is resolved into sulphate of ammonia and free valerianic acid. (Schlieper.)

$$C^{10}NH^9 + 4HO = NH^3 + C^{10}H^{10}O^4.$$

Nitric acid, hydrochloric acid, and ammonia have no action upon it. (Schlieper). — 4. With aqueous fixed alkalis, it is resolved with perfect facility into a valerate of the alkali and free ammonia (Schlieper, Guckelberger);— 5. It is decomposed at ordinary temperatures by potassium, into cyanide of potassium, hydrogen gas, and a peculiar hydrocarbon. (Dumas, &c.)

*Combinations.* Valeronitrile dissolves with tolerable facility in *water* (Schlieper) in about four times its volume of water. (Guckelberger.)

It mixes in all proportions with *alcohol* and *ether.* (Guckelberger.)

*Appendix to Valeronitrile.*

## Valeracetonitrile.

SCHLIEPER. (1846.) *Ann. Pharm.* 59, 12.

Produced in the preparation of valeronitrile from gelatin, in larger quantities than the valeronitrile itself, and passes over first in the rectification of the oil after dehydration by chloride of calcium (p.121), especially between 68° and 90°. The valeracetonitrile may be freed from admixed valeronitrile by rectifying it again, and collecting only that which passes over up to 76°, and then once more, collecting only up to 71°.

Transparent, colourless, strongly refracting, thin liquid, of sp. gr. 0·79; boils between 68° and 71°; leaves upon paper a grease-spot which quickly disappears; smells like valeronitrile but much more agreeably ethereal.

| | | | Schlieper. |
|---|---|---|---|
| 26 C | 156 | 60·93 | 61·35 |
| 2 N | 28 | 10·94 | 9·42 |
| 24 H | 24 | 9·38 | 11·40 |
| 6 O | 48 | 18·75 | 17·83 |
| $C^{26}N^2H^{24}O^6$ | 256 | 100·00 | 100·00 |

[The equation given by Schlieper for this formula, which does not quite agree with the analysis, viz.:

$$4C^{10}H^{10}O^4 + 3C^4H^4O^4 + 4NH^3 - 16HO = 2C^{26}N^2H^{24}O^6,$$

is very improbable.]

*Decompositions.* 1. Valeracetonitrile is easily set on fire, and burns with a faintly luminous flame. — 2. When chlorine gas is passed through it, a large quantity of hydrochloric acid is evolved, and the liquid becomes heated, and, if left in the cold, deposits white crystals of a chlorine-compound. — 3. With bromine, in a closed bottle occasionally opened, it gradually forms a bromine-compound which crystallizes in needles, and another which is liquid and has a terrible odour, attacking the nose and eyes. — 4. It is decomposed by oil of vitriol, yielding sulphate of ammonia, valerianic acid, and acetic acid. — 5. With aqueous fixed alkalis also, it is resolved, even at ordinary temperatures, into valerate and acetate of the alkali, and free ammonia.— Nitric acid, hydrochloric acid and ammonia do not exert any decomposing action upon it.

*Combinations.* It dissolves in *water* much more copiously than ether.

Mixes in all proportions with *alcohol* and *ether*. (Schlieper.)

*Conjugated Compounds.*

## Amyl-urea.

$$C^{12}N^2H^{14}O^2 = C^2(C^{10}NH^{12})Ad,O^2 = C^{10}(C^2NH^4)AdH^8,O^2.$$

WURTZ. (1851.) *Compt. rend.* 32, 417.

Produced in small quantity in the decomposition of allophanate [cyanurate] of amyl by ammonia. Decomposed by heated potash-ley into amylamine and carbonate of potash. Forms with nitric acid, crystals which are permanent in the air. (Wurtz.)

Wurtz has likewise obtained an ethamylurea = $C^{16}N^2H^{18}O^2$.

## ¶ Valeryl-urea.

$$C^{12}N^2H^{12}O^4 = C^2(C^{10}NH^{10}O^2)Ad,O^2 = C^{10}(C^2NH^2O^2)AdH^8,O^2.$$

N. Zinin. *J. pr. Chem.* 62, 355; *N. Ann. Chim. Phys.* 44, 57.
F. Moldenhauer. *Ann Pharm.* 94, 100.

Obtained by the action of chloride of valeryl on urea. (Zinin, Moldenhauer.) The action requires the aid of heat, being scarcely perceptible at ordinary temperatures. (Zinin.)

The compound resembles acetyl-urea (ix, 292), but is less soluble. (Zinin.) Deposited from the hot aqueous solution in microscopic laminæ having a pearly lustre, and soft and unctuous to the touch. The alcoholic solution yields slender needles, which under the microscope, appear like transparent four-sided prisms. Melts at 191°, and when carefully heated in a tube, yields a crystalline sublimate of broad iridescent laminæ. It is nearly insoluble in cold water and alcohol. (Moldenhauer.)

| | | | Moldenhauer. |
|---|---|---|---|
| 12 C | 72 | 50·00 | 49·57 |
| 2 N | 28 | 19·45 | |
| 12 H | 12 | 8·33 | 8·79 |
| 4 O | 32 | 22·22 | |
| $C^{10}N^2H^{12}O^2$ | 144 | 100·00 | |

May be regarded as $C^2N^2(H^3,C^{10}H^9O^2)O^2$.

It was not found practicable, by acting upon this compound with chloride of valeryl to replace a second atom of hydrogen in urea by valeryl. (Moldenhaur.) ¶.

## ¶ Amylopiperidine.

$$C^{20}NH^{21} = C^{10}H^{10},C^{10}NH^{11} = C^{10}NH^{10}(C^{10}H^{11})$$

Cahours. *N. Ann. Chim. Phys.* 88, 76; *Chem. Soc. Qu. J.* 6, 181.

Obtained by the action of iodide of amyl on piperidine. (x, 448.) Scarcely any action takes place at ordinary temperatures; but the mixture soon solidifies when heated in sealed tubes placed in the water-bath; and if, after the action has gone on for some days, the crystals are dissolved in a small quantity of water, and the liquid distilled in contact with fragments of caustic potash, amylopiperidine passes over in the form of a limpid liquid, the odour of which is both ammoniacal and amylic. After drying over fused potash, it is colourless and boils at 186°. Vapour-density = 5·477.

| | | | | | Cahours. |
|---|---|---|---|---|---|
| 20 C | 120 | .... | 77·41 | ........ | 77·54 |
| N | 14 | .... | 13·55 | ........ | 13·64 |
| 21 H | 21 | .... | 9·04 | ........ | 9·17 |
| $C^{20}NH^{21}$ | 155 | .... | 100·00 | ........ | 100·35 |

| | Vol. | | Density. |
|---|---|---|---|
| C-vapour | 20 | ........... | 9·3200 |
| N-gas | 1 | ........... | 0·9706 |
| H-gas | 21 | ........... | 1·4553 |
| | 2 | ........... | 11·7459 |
| | 1 | ........... | 5·8729 |

Amylopiperidine is less soluble in *water* than the corresponding methyl and ethyl-compounds. (x, 450, 451.)

The *Hydriodate* $C^{20}NH^{21},HI$ forms large white shining laminæ.

*Platinum-salt*.— $C^{20}NH^{21},HCl,PtCl^2$.— When bichloride of platinum is poured into a hot aqueous solution of amylopiperidine, dark, orange-coloured oily drops are deposited, which solidify in a few hours, presenting a crystalline aspect. On dissolving this product in dilute alcohol and evaporating slowly, the platinum-salt separates in very hard prisms, often of considerable size and of a fine orange colour, even when the quantity of material operated upon is very small. (Cahours.) ¶.

*Appendix to the Amylene-series*

## 1. Cacodyl of Valerianic Acid.

When valerate of potash is distilled with an equal weight of arsenious acid, a heavy, oily, slightly yellow liquid passes over, which has a penetrating, disagreeable, alliacious odour, fumes strongly in the air; but does not take fire spontaneously. With corrosive sublimate it forms a thick white precipitate, the alliaceous odour disappearing at the same time, and being replaced by an aromatic odour something like that of valerate of amyl. The oily liquid is soluble in water, and appears to reduce oxide of mercury. When kept for some time in an imperfectly closed vessel, it is entirely converted into a mass of large, hard, shining, four-sided prisms, which are nearly colourless, and after pressure between paper, inodorous: they have an acid reaction, dissolve in water, and are completely decomposed by oxide of silver. (W. Gibbs, *Sill. Am. J.* [2], 15, 118; *Ann. Pharm.* 86, 222.)

## 2. Stibamyls.

F. Berle. *J. pr. Chem.* 65, 385; *Ann. Pharm.* 97, 316; *Chem. Soc. Qu. J.* 9, 282.

These compounds are formed by the action of iodide of amyl on antimonide of potassium. The latter substance (prepared by Löwig's

process, ix, 79) is finely pulverised, with addition of about half its bulk of dry sand; then introduced into glass flasks, in such quantity as to fill them to about two-thirds, and iodide of amyl added sufficient to moisten the mass throughout. After some time, and generally not till after the application of heat, a violent action takes place, attended with volatilisation of the excess of iodide of amyl, which may be condensed by surmounting the flask with a distillation-tube. The flasks are then corked, their contents (a grey, pulverulent, coherent mass,) softened when cold with a small quantity of water, and emptied into a capacious cylinder, previously filled with carbonic acid gas. In this vessel, the product is repeatedly exhausted with ether; the ethereal solution, after it has become clear by standing, poured into a large flask filled with carbonic acid, and completely distilled off after addition of water or ether. The residue consists of *stibtriamyl*, protected from the action of the air by the water which is still present.

If the stibtriamyl, prepared as above, is contaminated with free amylic alcohol (as when the iodide of amyl used in the preparation is impure) or with iodide of amyl, the following method may be adopted for the preparation of pure compounds. The impure stibtriamyl is dissolved in a mixture of ether and alcohol; bromine in alcoholic solution carefully added till its colour just begins to be permanent; then the bromide of stibtriamyl precipitated by addition of a large quantity of water; the bromide converted into oxide of stibtriamyl, by means of silver-oxide suspended in alcohol; the resulting solution again precipitated by water; the separated oxide dissolved in hydrochloric acid and alcohol; the pure chloride precipitated by another addition of water, and freed from a small quantity of water by continued heating at 100°, and the use of chloride of calcium.

Pure *stibtriamyl* is a transparent, slightly yellowish liquid, very viscid below 20°, more mobile at higher temperatures. Has a peculiar aromatic odour, and a bitter, somewhat metallic and very persistent taste. Sp. gr. = 1·1333 at 17°. In contact with the air, it fumes strongly, but does not take fire; it decomposes at the same time, with separation of a white powder. A drop of it placed on a piece of bibulous paper, and exposed to the air, becomes so strongly heated that the paper-fibre is charred. In presence of very small quantities (2 per cent.) of amylic alcohol or iodide of amyl, stibtriamyl is also decomposed on exposure to the air, but without fuming or sensible rise of temperature. It is insoluble in water; sparingly soluble in absolute alcohol; very easily soluble in ether. Heated for eight days with iodide of amyl in a sealed glass tube placed in the water-bath, it does not show any inclination to combine.— [According to Cramer (*Pharm. Centr.* 1855, 465), stibtriamyl is a transparent, tolerably mobile liquid, having a disagreeable alliaceous odour which excites coughing. Its sp. gr. is 1·0587. It is insoluble in water; but dissolves readily in alcohol and ether. It fumes in the air without taking fire, and forms (by evaporation of the ethereal solution?) a transparent bitter, varnish-like mass which ultimately solidifies.]

| *Stibtriamyl.* | | | Berlé. | | |
|---|---|---|---|---|---|
| 30 C | 180 | 52·63 | 53·55 | 52·56 | 51·66 |
| 33 H | 33 | 9·65 | 10·00 | 10·00 | 10·00 |
| Sb | 129 | 37·72 | | | |
| $(C^{10}H^{11})^3Sb$ | 342 | 100·00 | | | |

Stibtriamyl combines with oxygen, iodine, &c., forming compounds, in which Berlé supposes 1 At. of the radical to be united with 2 At. of oxygen, &c.; the same view, in fact, as that proposed by Löwig for the compounds of stibethyl (ix, 80). — For another view of the constitution of the compounds of metalliodal radicals, containing 1 At. metal to 3 At. of an alcohol-radical, see x, 523.

*Oxide of Stibtriamyl* is produced by slow evaporation of an ethereal solution of stibtriamyl in contact with the air. There then remains a greyish-yellow, very viscid, resinous mass, which becomes somewhat more fluid when heated, but readily decomposes at a higher temperature. Tastes and smells like stibtriamyl. Insoluble in water; sparingly soluble in hydrated alcohol and in ether; easily soluble in absolute alcohol. The alcoholic solution precipitates the oxides of the heavy metals from their salts. It dissolves readily in acids, and the resulting componnds are precipitated from their alcoholic solutions by water.

*Chloride of Stibtriamyl.*—As obtained by dissolving the oxide in hydrochloric acid, or by the method already described (p. 126), it is a yellowish, translucent liquid, viscid at ordinary, comparatively mobile at higher temperatures, heavier than water; dissolves in alcohol and ether. When precipitated from the alcoholic solution by water, it obstinately retains small portions of water and alcohol, from which it can only be freed by continued heating to 100°, and drying over chloride of calcium. Has a peculiar smell and taste, like the radical. Decomposes above 160°.

| | | | Berlé. | |
|---|---|---|---|---|
| Sb | 129 | 31·23 | | |
| 30 C | 180 | 43·69 | 44·59 | 43·63 |
| 33 H | 33 | 8·09 | 8·2 | 9·00 |
| 2 Cl | 70 | 16·99 | 116·83 | |
| $(C^{10}H^{11})^3Sb,Cl^2$ | 412 | 100·00 | | |

*Iodide of Stibtriamyl* is obtained by dissolving the oxide in hydriodic acid and precipitating by water, or by adding iodine to the radical as long as it is decolorised. Very much like the chloride. *Bromide of Stibtriamyl* is prepared in like manner, and exhibits similar properties.

| *Iodide.* | | | Berlé. |
|---|---|---|---|
| Sb | 129 | 21·65 | |
| 30 C | 180 | 30·20 | 29·28 |
| 33 H | 33 | 5·54 | 6·10 |
| 2 I | 126 | 42·61 | 40·00 |
| $(C^{10}H^{11})^3Sb,I^2$ | 468 | 100·00 | |

| *Bromide.* | | | Berlé. |
|---|---|---|---|
| Sb | 129 | 25·70 | |
| 30 C | 180 | 35·86 | 36·04 |
| 33 H | 33 | 6·57 | 6·75 |
| 2 Br | 160 | 31·87 | 32·28 |
| $(C^{10}H^{11})^3Sb,Br^2$ | 502 | 100·00 | |

When chloride or iodide of stibtriamyl is mixed with an alcoholic solution of nitrate of silver, as long as a precipitate forms, and then

filtered, the filtrate forms an emulsion from which, after standing for some time in a warm place, two liquids separate; the upper being light, yellow and mobile, and the lower a deep brown-red oil. The upper layer, when slowly evaporated, yields slender white crystals grouped in stars; they may be purified by recrystallisation from dilute alcohol. The dark red oil likewise dissolves on addition of a large quantity of hydrated alcohol, and the solution, after standing for some time, yields the same crystals. These crystals melt at about 20 ; the fused mass does not dissolve in alcohol so readily as the crystals. This salt, the only crystallisable compound of stibtriamyl, is the *Nitrate of Sibtriamyl*, $(C^{10}H^{11})^3Sb,2NO^6$, (nitric acid by analysis 23·39 per cent; by calculation 22·30); it is insoluble in water and ether, but dissolves in hydrated alcohol. Has a peculiar metallic taste.

By decomposing equivalent quantities of sulphate of silver and a haloid compound of stibtriamyl, dissolved in alcohol, *Sulphate of Stibtriamyl* is obtained in solution. This salt was obtained only as an oily body, which yielded 18·03 per cent. sulphuric acid; the formula $(C^{10}H^{11})^3Sb,2SO^4$ requires 18·26 per cent.

The white powder, formed by the action of the air upon stibtriamyl, is insoluble in ether, alcohol, and water; it does not dissolve in hydrochloric acid, but imperfectly in fuming nitric acid; slowly in aqua-regia. It remains unaltered even when strongly heated, not decomposing below a red heat. Berlé supposes it to be $(C^{10}H^{11})^3Sb,2SO^4 + 2SbO^3$. When sulphuretted hydrogen was passed for some time through this compound suspended in alcohol, a white powder immediately separated, which gradually assumed an orange colour, and then formed a pulpy mass, which could not be filtered. After addition of a large quantity of alcohol and ether, the liquid, when left to stand in a warm place, deposited an orange-red, flocculent precipitate, which, after drying, formed a brownish-yellow powder, insoluble in alcohol, ether, and water; this powder decomposed at a very high temperature, and took fire when fuming nitric acid was poured upon it. Berlé regards this compound as $(C^{10}H^{11})^3SbS^2 + 2SbS^3$ (it gave 18·38 per cent. sulphur, the formula requiring 17·59). A compound, supposed to be identical with this, is formed by passing sulphuretted hydrogen for some time through an alcoholic solution of oxide of stibtriamyl.

*Stibbiamyl.* — When the product of the action of iodide of amyl upon iodide of potassium, instead of being exhausted with ether, was distilled in an atmosphere of carbonic acid, a liquid passed over, which was freed from undecomposed iodide of amyl by distillation over antimonide of potassium. The liquid thus obtained gave off when heated to 80°, a colourless gas, which had a peculiar odour; burnt with a bright flame diffusing a white smoke of antimonic oxide; was not absorbed by water; but when left for some time in contact with it, deposited a white coating of antimony on the sides of the vessel. After the gas had been driven off, the liquid was greenish yellow, had a peculiar aromatic odour and bitter taste; was tolerably mobile, and heavier than water. It was insoluble in water, but miscible in all proportions with alcohol and ether. Exposed to the air, it does not fume or become heated; when set on fire it burns with a very bright flame, diffusing a white fume of antimonic oxide; when heated in pure oxygen gas, it explodes with the greatest violence; fuming nitric acid decomposes it with considerable evolution of heat. This compound is *Stibbiamyl.*

| | | | | Berlé. | | |
|---|---|---|---|---|---|---|
| Sb | 129 | .... | 47·6 | | | |
| 20 C | 120 | .... | 44·3 | 45·13 | 43·30 | 44·83 |
| 22 H | 22 | .... | 8·1 | 8·80 | 9·01 | 8·60 |
| $(C^{10}H^{11})^2Sb$ | 271 | .... | 100·0 | | | |

When an ethereal solution of stibbiamyl is left to evaporate in the air, the resulting oxide absorbs carbonic acid. The radical heated for some time to 100° in a stream of dry carbonic acid, yielded a liquid similar in properties to the pure radical, but more viscid. This liquid gave 42·19 per cent. carbon, and is regarded by Berlé as $(C^{10}H^{11})^2SbO,CO^2$, this formula requiring 41·52 per cent. C. The haloid salts of stibbiamyl are gummy liquids; the sulphate and nitrate are precipitated from their alcoholic solutions by water in the form of gummy masses, which dry up to amorphous solids.

[According to Werther (*J. pr. Chem.* 64, 505), the product obtained by the action of iodide of amyl on antimonide of potassium in an atmosphere of carbonic acid, cannot be distilled without decomposition: but by extracting the mass with ether, a solution is obtained, which, when left to evaporate in the air, appears to form the oxides of two radicals, one soluble and the other insoluble in ether; both yield crystallisable salts.]

## Zinc-amyl. $C^{10}H^{11}Zn$.

FRANKLAND. *Ann. Pharm.* 85, 360; *Chem. Soc. Qu. J.* 6, 64.

Produced by the action of zinc on iodide of amyl at 180°.

$$[C^{10}H^{11}I + 2Zn = ZnI + C^{10}H^{11}Zn.]$$

It is a colourless transparent liquid, which fumes in the air, but does not take fire. By water it is resolved into oxide of zinc and hydride of amyl.

$$C^{10}H^{11}Zn + HO = ZnO + C^{10}H^{11},H.$$

## 3. Stannamyls.

A. GRIMM. *J. pr. Chem.* lxii. 385; *Ann. Pharm.* 92, 383.

*Formation and Preparation.* By the action of iodide of amyl on stannide of sodium. — Iodide of amyl acts with violence on an alloy of 1 pt. sodium and 6 pts. tin (ix, 92), especially if the iodide contains amylic alcohol, and the stannide of sodium is not mixed with sand. About 2½ or 3 oz. of stannide of sodium is quickly pounded in an iron mortar with twice its weight of sand; the mixture immediately introduced into a glass flask of 5 or 6 times its bulk, and sufficient iodide of amyl added to form a pasty mass; a distillation-tube then adapted to the flask; and the mixture left to stand for some minutes. If no action takes place at ordinary temperatures, the flask must be heated in the water-bath, but removed as soon as the materials begin to act; the action then

goes on rapidly and with so much evolution of heat, that the excess of iodide of amyl distils over completely. The flask is then to be closed while still hot, and the same process is pursued with several other flasks. The dry, yellow, pulverulent mass, which remains in the flasks after cooling, is then introduced into a bottle filled with ether and shaken up strongly several times, and the whole left to stand, without closing the vessel air-tight, till the ether separates quite clear. The ethereal solution is then decanted and the residue repeatedly treated with ether, as long as that liquid extracts any thing from it. The ethereal solution thus formed contains the following radicals: *Stannamyl*, $C^{10}H^{11}Sn$; *Bistannamyl* $C^{10}H^{11}Sn^2$; *Methylene-stannamyl* $(C^{10}H^{11})^2Sn^2$; *Methstannamyl* $(C^{10}H^{11})^3Sn^2$; *Methstannbiamyl* $(C^{10}H^{11})^4Sn^2$. These compounds may be separated by either of the following methods:

A. The ethereal solution is mixed with alcohol and the ether distilled off; the alcoholic solution when cold, decanted from the matter which has separated out, then saturated with iodine, and the iodide of *Methstannbiamyl* extracted with ether; the whole of the radical of this compound remains in the alcoholic solution. The mass which separates out is next dissolved in ether; the ethereal solution saturated with iodine; the ether distilled off; and the residue dissolved in absolute alcohol. The alcoholic solution is now poured, with agitation, into potash-ley, which must not be in too great excess, whereupon a white unctuous mass is precipitated, consisting of a mixture of the oxides of *bistannamyl, methylene-stannamyl* and *stannamyl*, while the oxide of *methstannamyl* remains for the most part dissolved in the alcohol. The precipitate, after separation from the liquid, is treated with ether, which dissolves the oxides of *bistannamyl* and *methstannamyl*, leaving undissolved the oxides of *stannamyl* and *methylene-stannamyl*. This insoluble residue is treated at a moderate heat with alcohol and a little sulphuric acid, whereupon the sulphate of *stannamyl* remains undissolved, while the sulphate of *methylene-stannamyl* passes into the alcoholic solution, and may be precipitated therefrom by water in the form of a tough mass which subsequently hardens. Or, the oxides may be treated with alcohol and hydrochloric acid, and the resulting solution left to evaporate: the chloride of *methylene-stannamyl* then crystallises out first. Lastly, the ethereal solution is distilled to expel the ether, and the residue treated with cold alcohol, which dissolves the oxide of *methstannamyl* and leaves undissolved the oxide of *bistannamyl*.

B. The ethereal solution, which contains the whole of the radicals and has been mixed with a little alcohol, is left to evaporate slowly in the air. The radicals then gradually oxidise, and the oxides of *stannamyl* and *methylene-stannamyl* separate out, while the rest remain in solution. The liquid is then diluted, and the residue again treated with alcohol, whereby the oxides of *methstannamyl* and *methstannbiamyl* are dissolved, while the oxide of *bistannamyl* remains for the most part undissolved. On saturating this alcoholic solution with hydrochloric acid and adding water drop by drop, the chloride of *methstannamyl* separates in a state of purity, while the chloride of *methstannbiamyl* dissolves with tolerable facility, even in hydrated alcohol.

*Properties.* The stannamyls in the free state are unctuous, non-volatile bodies which do not possess any very characteristic odour. They are insoluble in water, but dissolves readily in ether. In alcohol they dissolve for the most part less readily in proportion as they contain more

tin. They are but little altered by exposure to the air, neither fuming nor taking fire. Fuming nitric acid oxidises them with great violence, generally causing strong detonation and projection of the mass, but without setting it on fire.—When the ethereal solution is left to evaporate in the air, the radicals quickly oxidise.— Bromine added drop by drop to the radicals, causes a violent reaction and considerable evolution of heat; this effect also takes place on the addition of bromine or iodine in alcoholic solution. — The oxides of all the stannamyls are separated from their salts by ammonia. Their solutions have a strong alkaline reaction. All the compounds of the stannamyls are non-volatile, and most of them inodorous. They exhibit for the most part, but little tendency to crystallise.

BISTANNAMYL. $C^{10}H^{11}Sn^2$.—The *oxide* is a perfectly transparent mass, having the consistence of turpentine, and brittle in the cold. It dissolves very sparingly in absolute alcohol, readily in ether and in a mixture of ether and alcohol.

The *chloride* is also a viscid, transparent mass, soluble in alcohol and ether. So likewise the *sulphate.*

| *Oxide.* | | | Grimm. |
|---|---|---|---|
| 2 Sn | 118 | 59·89 | 58·92 |
| $C^{10}H^{11}$ | 71 | 36·04 | |
| O | 8 | 4·07 | |
| $C^{10}H^{11}Sn^2,O$ | 197 | 100·00 | |

| *Chloride.* | | | Grimm. |
|---|---|---|---|
| 2 Sn | 118·0 | 52·56 | |
| $C^{10}H^{11}$ | 71·0 | 31·63 | |
| Cl | 35·4 | 15·81 | 15·48 |
| $C^{10}H^{11}Sn^2,Cl$ | 224·4 | 100·00 | |

STANNAMYL.— $C^{10}H^{11}Sn$. [Likewise obtained by Frankland. (*Chem. Soc. Qu. J.* 6, 62).] The *oxide* is a dazzling white, amorphous, inodorous powder, nearly insoluble in ether, somewhat soluble in boiling alcohol. Gave by analysis 40·15 and 42·53 p. c. tin, the formula $C^{10}H^{11}SnO$ requiring 42·75.

The *chloride* is, above 15°, a thick transparent oil, but solidifies into a crystalline mass between 4° and 5°. It has a faint odour, like that of camphor, is unctuous to the touch, and burns with a bright, green-edged flame. Dissolves readily in alcohol and ether.

| *Chloride.* | | | Grimm. |
|---|---|---|---|
| Sn | 59·0 | 35·65 | 34·20 |
| 10 C | 60·0 | 36·25 | 37·79 |
| 11 H | 11·0 | 6·65 | 6·72 |
| Cl | 35·4 | 21·45 | 20·26 |
| $C^{10}H^{11}SnCl$ | 165·4 | 100·00 | 98·97 |

*Sulphate,* $C^{10}H^{11}SnO,SO^3$. — White amorphous powder insoluble in water and ether, sparingly soluble in alcohol. Gave by analysis 21·90 and 21·98 p. c. $SO^3$, the formula requiring 22·47 p. c.

METHYLENE-STANNAMYL. $(C^{10}H^{11})^2Sn^2$.—The *oxide* resembles that of stannamyl. Gave 43·87 and 44·10 and in another preparation, 43·82 p. c. tin, while the formula $(C^{11}H^{11})^2Sn^2,O$ requires 44·03 p. c.

*Chloride.* — Separates from the alcoholic solution in distinct prismatic crystals, which melt at 70° into an oily liquid, and solidify again in a crystalline mass on cooling. Smells somewhat stronger than the chloride of stannamyl. Less soluble in alcohol.

| | | | Grimm (*mean*). |
|---|---|---|---|
| 2 Sn | 118·0 | 39·93 | 39·33 |
| 20 C | 120·0 | 40·60 | 39·63 |
| 22 H | 22·0 | 7·45 | 7·70 |
| Cl | 35·4 | 12·02 | 11·53 |
| $(C^{10}H^{11})^2Sn^2,Cl$ | 295·4 | 100·00 | 98·19 |

*Sulphate.* — $(C^{10}H^{11})^2Sn^2O,SO^3$. — Remains as an amorphous mass, when the alcoholic solution is evaporated. Dissolves readily in alcohol, and is separated from the solution by water in the form of a white flocculent powder, which at 100° cakes together in a resinous mass. Analysis gave 13·14 p. c. sulphuric acid, the formula requiring 12·99 p. c.

METHSTANNAMYL. $(C^{10}H^{11})^3Sn^2$.—The *oxide* is obtained by shaking up the ethereal solution of the chloride with a small quantity of alcoholic potash-solution, then adding a large quantity of water, and leaving the ethereal solution of the oxide which then separates, to evaporate.

The *chloride* is a faintly yellow transparent oil, which is insoluble in water, readily soluble in alcohol, and may be precipitated therefrom by water.

| *Oxide.* | | | Grimm. |
|---|---|---|---|
| 2 Sn | 118 | 34·80 | 35·43 |
| 30 C | 180 | 53·09 | 52·36 |
| 33 H | 33 | 9·74 | 9·51 |
| O | 8 | 2·37 | 2·70 |
| $(C^{10}H^{11})^3Sn^2O$ | 339 | 100·00 | 100·00 |

| *Chloride.* | | | Grimm. |
|---|---|---|---|
| 2 Sn | 118·0 | 32·19 | 32·30 |
| 30 C | 180·0 | 48·83 | 47·31 |
| 33 H | 33·0 | 9·31 | 10·36 |
| Cl | 35·4 | 9·67 | 9·24 |
| $(C^{10}H^{11})^3Sn^2Cl$ | 366·4 | 100·00 | 99·21 |

*Sulphate.* $(C^{10}H^{11})^3Sn^2O,SO^3$. — Obtained by adding sulphuric acid to the alcoholic solution of the oxide; then precipitating by water; washing the precipitate with water; redissolving it in alcohol; and leaving the solution to evaporate. The salt then remains in the form of a transparent amorphous mass, which dissolves pretty easily both in alcohol and ether. Contains 10·82 p. c. sulphuric acid (calculation 10·35).

METHSTANNBIAMYL. $(C^{10}H^{11})^4Sn^2$. — Colourless oily liquid readily soluble in alcohol and ether.

*Oxide.* — Colourless, mobile oil easily soluble in alcohol, and having a pleasant odour like that of jasmine.

| | | | | Grimm. | |
|---|---|---|---|---|---|
| 2 Sn | 118 | .... 28·78 | ........ 29·33 | .... 29·21 |
| 40 C | 240 | .... 58·54 | ........ 58·05 | .... 57·05 |
| 44 H | 44 | .... 10·73 | ........ 10·64 | .... 10·01 |
| O | 8 | .... 1·95 | ........ 1·98 | .... 3·73 |
| $(C^{10}H^{11})^4Sn^2,O$ | 410 | .... 100·00 | ........ 100·00 | .... 100·00 |

*Chloride.* $(C^{10}H^{11})^4Sn^2,Cl$.— Colourless oil, soluble in alcohol even if hydrated, but precipitated from the solution on addition of a larger quantity of water. Gave by analysis 8·33 and 8·20 p. c. chlorine (calculation, 8·11 p. c.)

*Iodide.*—Crystallises at low temperatures, but melts easily into an oily liquid. (Grimm.)

| | | | Grimm. |
|---|---|---|---|
| 2 Sn | 118 | .... 22·34 | ........ 22·27 |
| 40 C | 240 | .... 45·46 | |
| 44 H | 44 | .... 8·33 | |
| I | 126 | .... 23·87 | ........ 23·68 |
| $(C^{10}H^{11})^4Sn^2,I$ | 528 | .... 100·00 | |

HYDRARGAMYL. — Iodide of amyl exposed to sunshine in contact with metallic mercury, yields a compound similar to iodide of hydrargomethyl. (Frankland, *Ann. Pharm.* 85, 204.) ¶.

# COMPOUNDS CONTAINING 12 AT. CARBON.

## BENZENE SERIES $C^{12}H^6$.

### Benzene. $C^{12}H^6$.

FARADAY. *Phil. Trans.* 1825, 440; also *Schw.* 47, 340 and 441; also *Pogg.* 5, 306.
MITSCHERLICH. *Berl. Ak. d. W.* 1834; abstr. *Pogg.* 29, 231; also *Ann. Pharm.* 9, 39.
PELIGOT. *Ann. Chim. Phys.* 56, 59.
MANSFIELD. *Chem. Soc. Qu. J.* 1, 244; also *Ann. Pharm.* 69, 162.

*Bicarburet of Hydrogen* (Faraday); *Benzin* (Mitscherlich); *Benzon* (Liebig); *Benzol, Phène* (Laurent); *Fune.* (Gm.)

*Formation.* 1. When benzoic acid is heated with excess of lime (Mitscherlich), or when its vapour is passed over red-hot iron. (D'Arcet, *Ann. Chim. Phys.* 66, 99.) — 2. By the dry distillation of kinic acid. (Wöhler.) — 3. By heating phthalic acid with lime. (Marignac, *Ann. Pharm.* 42, 217.) — 4. By passing bergamot-oil over red-hot lime. (Ohme, *Ann. Pharm.* 31, 318.) — 5. By passing fats through red-hot tubes. (Faraday.) — 6. By the dry distillation of coal. (Hofmann, Mansfield.) A good process for finding benzol in such products of distillation, is given by Hofmann. (*Ann. Pharm.* 55, 201.)

*Preparation.* 1. A mixture of 1 pt. benzoic acid and 3 pts. of slaked lime is distilled at a gently increasing heat; and the oily benzol which has passed over is separated from the water, and rectified after being shaken up with a little potash. 3 pts. of benzoic acid yield 1 pt. of benzene. (Mitscherlich.)

2. The benzene obtained in the preparation of butylene (x, 66), still retains a certain quantity of the oil $C^{12}H^8$; to free it from this impurity, it must be melted; then, after solidification at $-18°$, repeatedly pressed upon paper with a glass rod, so as to make the oil soak into the paper; then melted again, and poured out into cakes in moulds of tin-foil: these pressed in a hydraulic press between several layers of filtering paper which has been dried by heat and left to cool; and finally deprived of all moisture by distillation over lime. (Faraday.)

3. *From Coal-tar.* The tar which passes over in the distillation of illuminating gas from coal, contains, according to Mansfield and others, variable quantities of the following substances: sulphuretted hydrogen; ammonia; hydrocyanic acid; acetic acid; an oil which boils between 60° and 70°, and becomes brown and resinous by oxidation; benzene; carbolic acid; aniline; picoline; pyrrol; an oil having the composition $C^{12}H^8$; toluene

$C^{14}H^8$; cumene $C^{18}H^{12}$; leucol; naphthalin $C^{20}H^8$ (in small quantity, approaching to $\frac{1}{4}$, according to the nature of the coal and the manner in which the process is conducted): cymene $C^{20}H^{14}$; chrysene, and anthracene.

The tar is black, viscid, and of specific gravity 1·12 to 1·15. When it is distilled on the manufacturing scale in large iron vessels, ammoniacal gas passes over first, then water containing ammoniacal products, and a yellow or brown mobile oil, of sp. gr. 0·900 to 0·950, and having a disagreeable odour proceeding from ammonia, picoline, &c.: this thin oil, the quantity of which continually increases in proportion to that of the water, is called *light oil, crude naphtha* or *light naphtha.* (It is purified in the manufactories by rectification, a portion of heavy naphtha (*vid. inf.*) still remaining in it; then by agitating the rectificate, — which is colourless at first, but has an offensive odour, and gradually turns brown from formation of resin, — with oil of vitriol, which thereby acquires a dark red colour; and again rectifying the coloured naphtha decanted therefrom. It is then colourless, free from naphthalin, and has no longer any unpleasant odour.)

By again distilling the coal-tar with a fresh receiver, a yellow stinking oil is obtained called *dead oil* or *heavy naphtha,* which sinks in water, yields more or less crystallised naphthalin, and contains leucol and anthracene, besides oily hydrocarbons boiling between 200° and 300°, and aniline. (It serves for common lamps and torches, for preserving wood used in building, and for the preparation of lamp-black.)

The residue which remains after the distillation of the heavy naphtha, and solidifies on cooling into a black mass called *Pitch* (used for the preparation of asphalt, and when dissolved in a small quantity of heavy naphtha, serving as a black iron-varnish), gives off, when still more strongly heated, first a buttery mass consisting chiefly of anthracene; then a yellowish more resinous distillate; and finally, when the iron retort becomes, heated to redness, an orange-yellow, inodorous powder, which feels glutinous between the fingers. In the retort there remains a very hard coke difficult to burn.

When the still impure light naphtha is distilled, its boiling point rises, beginning at 100° and ultimately attaining 200° to 220°. The last distillate generally yields crystals of naphthalin; the residual black brown mass, different from pitch, and consisting chiefly of oils resinised by oxidation, yields, when more strongly heated, a distillate containing, besides a little water, a red oil having a very peculiar odour, but little or no anthracene.

When the light naphtha is several times alternately shaken up with dilute sulphuric acid, washed with water, agitated with dilute potash; washed with water, agitated with sulphuric acid, &c. &c. till it is freed from all basic and acid impurities, it appears but little diminished; but has lost the greater part of its disagreeable odour; and no longer colours clean fir-wood yellow (as when it contained aniline), or firwood moistened with hydrochloric acid purple (from containing pyrrhol); and no longer destroys the cuticle. When thus purified, it begins to boil at about 100° about $\frac{2}{3}$ of it distilling over at 150°, and the greater part of the remaining $\frac{1}{3}$ at 200°, the portion which distils over near 200°, sinking in water and solidifying as it cools. If in this distillation, the receiver be changed at every 5°, and each of the resulting distillates rectified by itself, also with change of receiver at every 5° (during which process, it is found that a distillate obtained at a certain temperature, *e.g.* at 110°

to 115°, begins to boil at a lower temperature, *e.g.* at 90°, and rises about 30° or 40° higher, *e.g.* to 120°); and if all the rectificates obtained at the same temperature are mixed together and again rectified, and the process continued in the same manner, till the whole has been ten times subjected to fractional distillation, the residues of which distillations are brown, especially at the beginning, — the boiling points exhibit distinct intervals, and there are obtained (after removal of the less volatile distillates which crystallise in consequence of containing naphthalin) five oils of different degrees of volatility, and smelling like rock-oil but yet differently one from the other, and of sp. gr. from 0·86 to 0·88; viz.

*A.* Oil boiling between 60° and 70°, smelling like garlic and sulphide of carbon, very small in quantity. It combines for the most part with oil of vitriol, and on addition of water, a solid aromatic substance separates. Perhaps a mixture of benzene, which crystallises out from it below — 20°, and two more volatile oils.

*B.* Oil boiling from 80° to 85°, amounting to $\frac{1}{16}$ of the light naphtha : Benzene.

*C.* Oil boiling from 110° to 115°; in large quantity. May be set on fire, even when cold, by contact with a flame; imparts to air passed through it at ordinary temperatures the property of burning with a blue flame. Consists chiefly of toluene $C^{14}H^8$.

*D.* Oil boiling from 140° to 145°. In large quantity. Behaves like cumene. Air passed through the cold oil is not rendered inflammable.

*E.* Oil boiling from 170° to 175°. Forms but a small portion of the light naphtha (but a large portion of the heavy naphtha.) It has a density of 0·857 and consists of cymol $C^{20}H^{14}$ (Mansfield; see also Ritthausen, *J. pr. Chem.* 61, 74).

*a.* To obtain merely the benzene, it is sufficient to repeat the above-described rectification five instead of ten times. The portion which distils over between 80° and 90° is left to crystallise at — 12°; thrown in a finely divided but closely pressed state on a strong cloth strainer which is fixed in a cylinder cooled to – 22°; and the air partially exhausted below the strainer by working a piston, so as to force the oil through it by atmospheric pressure : a Beart's coffee-machine is very well adapted to the purpose. The still impure benzene which remains on the filter in the form of a snowy crystalline mass, is left to thaw gradually (the last portion generally melts at + 4° to + 5°); the remaining liquid, which becomes continually poorer in foreign oils, collected in several bottles placed one after another below the funnel; and each of these fractions left to freeze by itself, and again fractionally thawed till the whole melts at + 4° to + 5°. (Mansfield.)

*b.* The portion of the light naphtha which passes over first in the distillation of the coal-tar, and therefore contains a smaller portion of the more fixed oils, is distilled from a metal still, and the vapours passed, first upwards into a chamber surrounded with water, (or into a worm tube), in which the oils that boil above 100° condense and run back, and then downwards into the cooling apparatus; and the resulting distillate rectified in the same manner, only that the temperature of the surrounding water is not allowed to rise above 80°, and the distillation stopped as soon as the heat in the retort begins to rise above 90°. This rectificate, only half of which solidifies at — 20°, is shaken up with one-fourth of its bulk of oil of vitriol (or better, first with $\frac{1}{10}$ of its bulk of strong nitric acid, and then, after decantation therefrom, with $\frac{1}{4}$ of oil of vitriol), and rectified (without separation from the oil of vitriol) till the

boiling point in the retort rises to 90°. If this rectificate, on being mixed with oil of vitriol, assumes a colour darker than straw-yellow, it must be again distilled with oil of vitriol, then washed with water and afterwards with an alkaline ley. The oil of vitriol frees the liquid from alkaloids, and oxidises the oil which turns brown and boils at 60° to 70°, but without acting on the benzene, even when heated. The nitric acid likewise purifies the liquid by oxidation: it is true that it produces a certain quantity of nitrobenzene, but this is left behind in the distillation. Lastly, the benzene is purified, as in the preceding process, by freezing, pressure, &c. (Mansfield.)

*Properties.* Crystalline in the cold, of sp. gr. 0·956; at − 18° it is nearly as hard as lump-sugar, brittle, and pulverulent; colourless and transparent; does not conduct electricity. (Faraday.) After slow solidification, it forms laminæ united in fern-like tufts: after rapid cooling, it resembles camphor or white crystalline wax. (Mansfield.) Melts at 5·5° (at 7°, according to Mitscherlich), expanding at the same time by $\frac{1}{16}$ of its bulk (Faraday), and solidifies again at 0° (Mitcherlich, Mansfield); in narrow vessels, however, it may be cooled considerably below 0° without solidifying, and then solidifies suddenly on being shaken or poured out. (Mansfield.) In the melted state, it is a thin oil; the bubbles which form on its surface when shaken quickly disappear: it refracts light strongly. (Mansfield.) Sp. gr. 0·85 at 15·5° (Faraday, Mitscherlich, Mansfield), 0·8991 at 0°. (Kopp.) — Boils at 80·4° under a pressure of 0·76 met. (Kopp, *Pogg.* 72, 223); between 80° and 81° (Mansfield); at about 82° (Peligot); at 85·5° (Faraday); at 86° (Mitscherlich); 80·8° (Church, *Phil. Mag. J.* [4], 9, 256), and volatilises undecomposed. Vapour-density = 2·752 (Faraday), 2·770 (Mitscherlich, Mansfield.) — Smells like the illuminating gas produced from fatty substances, and somewhat like bitter almonds. (Faraday.) Its vapour does not produce narcotic effects when inhaled. (Snow.)

| | | | Faraday. | Mitscher-lich. | Peligot. | D'Arcet. | Dumas & Stas. | Kopp. | Nichol-son. |
|---|---|---|---|---|---|---|---|---|---|
| 12 C | 72 | 92·31 | 91·72 | 91·62 | 92·87 | 92·07 | 92·2 | 91·92 | 92·3 |
| 6 H | 6 | 7·69 | 8·30 | 7·76 | 7·73 | 7·93 | 7·7 | 7·76 | 7·7 |
| $C^{12}H^6$ | 78 | 100·00 | 100·02 | 100·38 | 100·60 | 100·00 | 99·9 | 99·68 | 100·0 |

| | Vol. | Density. |
|---|---|---|
| C-vapour | 12 | 4·9920 |
| H-gas | 6 | 0·4158 |
| Vapour of Benzene | 2 | 5·4078 |
| | 1 | 2·7039 |

*Decompositions.* 1. The vapour passed through *a red-hot tube* is converted, with gradual deposition of charcoal, into a gaseous hydrocarbon. (Faraday.) The oil is very inflammable and *burns* with a bright, very smoky flame. (Faraday.) Solid benzene burns when set on fire, without previous fusion. (Mansfield.) Benzene volatilising in oxygen gas at ordinary temperatures, forms a mixture which explodes violently when an electric spark is passed through it. 2 vol. benzene-vapour consume in this manner 15 vol. oxygen-gas, 12 vol. of which with 12 vol. carbon-vapour form 12 vol. carbonic acid gas, and the remaining 3 vol. with

6 vol. hydrogen form water. (Faraday.) Air charged with benzene-vapour, burns from a jet with a white smoky flame or with a violet flame, according to the width of the jet and the velocity of the stream; hydrogen gas charged with benzene vapour burns in a similar manner with a bright white flame. (Mansfield.) — 3. Benzene immersed in *chlorine-gas* and exposed to the sun, is converted, with rise of temperature and formation of hydrochloric acid, into crystals and an oil. (Faraday.) The oil consists of terchlorobenzene and the crystals of hydrochlorate of terchlorobenzene (Mitscherlich); according to Peligot, this transformation does not take place in the dark. — 5. *Bromine* dissolved in benzene likewise acts upon it only in sunshine, forming hydrobromate of terbromobenzene. (Mitscherlich.) Iodine does not act upon benzene even in sunshine. (Faraday.) — 6. Moderately strong *nitric acid* has no action upon benzene even when distilled with it; but in the warm fuming acid, it dissolves, with evolution of heat, forming nitrobenzene, $C^{12}XH^5$, which partly separates in the form of an oil on cooling. (Mitscherlich.) Faraday observed reddening and an odour of hydrocyanic acid. According to Abel, benzene is ultimately converted into nitrobenzene, by repeated distillation even with dilute nitric acid. — 7. Cold anhydrous *sulphuric acid* converts benzene, with moderate rise of temperature and without evolution of sulphurous acid, into a viscid liquid, consisting of 5 to 6 per cent. of sulphibenzene $C^{12}H^5SO^2$, benzosulphuric acid, $C^{12}H^6,2SO^3$, and another acid, which forms a non-crystallisable salt with oxide of copper. With fuming oil of vitriol, the same products are formed; the sulphibenzene however amounting to only 1 or 2 per cent. — Formation of sulphibenzene:

$$C^{12}H^6 + SO^3 = C^{12}H^5SO^2 + HO.$$

Common oil of vitriol has no action upon it. (Mitscherlich.) — The following substances have no action upon benzene: iodine in sunshine; potassium and aqueous alkalis at the boiling point of benzene (Faraday); non-fuming oil of vitriol even at the boiling point of benzene (Mitscherlich, Mansfield); aqueous chromic acid (Abel); phosgene-gas in sunshine (Mitscherlich); pentachloride of phosphorus. (Cahours.)

*Combinations.* Benzene dissolves very sparingly in *water*, imparting a strong odour to it. (Mitscherlich.)

It dissolves small quantities of *phosphorus, sulphur*, and *iodine* (the last with crimson colour: Faraday), more at a boiling heat, the excess separating on cooling. (Mansfield.)

It dissolves *bromine.* (Mansfield.)

It dissolves in *wood-spirit.* (Mansfield.)

It dissolves very sparingly in *alcohol*, and is separated therefrom by water. (Faraday.) A mixture of 1 vol. benzene and 2 vol. alcohol of sp. gr. 0·85 gives a good light in lamps; but an addition of alcohol makes the flame duller, and an addition of benzene, more smoky. (Mansfield.)

It dissolves very sparingly in *ether.* (Faraday, Mitscherlich.)

It dissolves readily in *acetone*, separating the water from that liquid if hydrated. (Mansfield.)

It dissolves large quantities of oils both fixed and volatile, (Faraday, Mansfield), also camphor, wax, mastic, caoutchouc and gutta percha, small quantities of gumlac, copal, anime and gamboge, a tolerably large quantity of quinine, small quantities of morphine and strychnine, but no cinchonine. (Mansfield.)

## Carbolic Acid.

$C^{12}H^6O^2 = C^{12}H^6,O^2.$

REICHENBACH. *Schw.* 66,301 and 345; 67, 1 and 57; 68, 352.
RUNGE. *Pogg.* 31, 69; 32, 308.
LAURENT. *N. Ann. Chim. Phys.* 3, 195; also *J. pr. Chem.* 25, 401.

*Creosote* (from κρέας, flesh and σώζειν, to preserve), *Phenol, Hydrate of Phenyl, Hydrated oxide of Phenyl, Phenic acid, Phenous acid, Spirol, Salicon* [*Nefune*]. — Reichenbach, obtained, in 1832, from wood-tar his creosote, and Runge in 1834, from coal-tar, his carbolic acid; Laurent also in 1841 obtained from coal-tar, his hydrate of phenyl, and gave a correct analysis of it. His investigations, as well as others of more recent date, showed that these three substances differ from one another only in their several degrees of purity. According to Gorup-Besanez (*Ann. Pharm.* 78,231, 86,223; 96, 39) creosote (apparently that which is prepared from beech-tar) is essentially different from Laurent's phenic acid, inasmuch as it gives different results by analysis and totally different products with chlorine and nitric acid. But to establish this point, he should have examined creosote prepared by himself, not that procured from a manufactory. Völckel also (*Ann. Pharm.* 86, 66) regards creosote as different from hydrate of phenyl, but assigns to it a formula different from that given by Gorup-Besanez. Lastly from the experiments of Williamson and Fairlie (*Chem. Soc. Qu. J.* 7, 232), it appears that coal-tar creosote contains, besides hydrate of phenyl, the homologous substance $C^{14}H^8O^2$ which may be separated by fractional distillation.

*Sources.* In castoreum (Wöhler), and in cows', horses'; and human urine. (Städeler, *Ann. Pharm.* 67, 360; 77, 17.)

*Formation.* By the dry distillation of wood (Reichenbach), of coal (Reichenbach, Runge, Laurent), of bones (Reichenbach), of gum benzoin (E. Kopp), of the resin of *Xantorrhœa hastilis* (Stenhouse), of salicylic acid (when rapidly heated), of alkaline salicylates and of saliretin (Gerhardt), of salicin with lime (Stenhouse), of kinic acid (Wöhler), of chromate of pelosin. (Bödeker.)

*Preparation.* 1. *From Beech-wood Vinegar.* — This substance contains from 1 to $1\frac{1}{2}$ per cent. of creosote, which rises to the surface as an oil, when the liquid is saturated with common salt or sulphate of soda. — The liquid is saturated by agitation with effloresced Glauber's salt at 70° to 80°, at which temperature it dissolves the largest quantity of that salt; the brown oil, amounting to 5 per cent. which rises to the surface, and consists of creosote, acetic acid, a small quantity of eupione and other oils, removed before it sinks to the bottom and mixes with the crystals of Glauber's salt; separated, after standing for several days in a cool place, from the acetic acid which rises to the surface, by removing the latter, and from the crystallising Glauber's salt by straining through linen; and then shaken up warm with carbonate of potash to free it from the remaining acetic acid. The oil which has been decanted from the alkaline liquid containing acetate of potash, and has become thicker, is distilled

with water from iron retorts, care being taken to avoid percussive ebullition and not to burn the copious brown residue; the pale yellow oil which has passed over and assumes a deep brown colour on exposure to the air, briskly agitated with very dilute phosphoric acid to extract the ammonia; the acid liquid then removed; the oil shaken up with fresh phosphoric acid; freed from the acid by repeated washing with water,—then again briskly agitated with an equal weight of warm dilute phosphoric acid; and distilled with this acid, the watery part of the distillate being repeatedly poured back, till but little more creosote passes over, and the oily residue is thrown about in the water in thickish lumps. (There still remain small quantities of acetate and phosphate of potash and ammonia.) The colourless oil which has passed over is further dissolved, after decantation of the watery distillate, in cold potash-ley of sp. gr. 1·12, the layer of eupione which rises to the surface when the liquid, milky at first, is left at rest, being removed, and freed from the remaining creosote by repeatedly washing it with a weaker solution till the eupione has become tastless; the whole of the solutions containing an impure compound of creosote and potash united; the mixture gradually heated to the boiling point in an open vessel, during which an admixed oil rapidly absorbs oxygen and becomes resinised; the mixture, which has become black-brown, treated, after cooling, with a sufficient quantity of sulphuric acid to set free all the creosote, which then exhibits a brown colour; and this creosote decanted while hot from the sulphate of potash, and distilled in a capacious glass retort, the distillation, however, not being continued to dryness or till the brown resinous residue begins to char: on this account the bottom of the retort should be surrounded with sand. The water contained in the creosote to the amount of 10 per cent. produces violent percussion during this process. This treatment with potash and sulphuric acid, and the distillation, are repeated from twice to four times, till the potash-solution, when heated in the air, no longer turns brown, but only slightly reddish. The creosote separated from this solution by sulphuric acid, is well washed with water and rectified, and potash-ley dissolved in it in just sufficient quantity to redden turmeric perceptibly, in order to keep back the remainder of any acid that may be present; the liquid then distilled over alcohol, as long as the creosote passes over without colour, at which stage of the process the residue amounts to about 4 or 5 times the volume of the potash-ley used; and the distillate, which should not turn brown even after several days' exposure to the air, several times rectified over alcohol, the anhydrous creosote which passes over after the percussive ebullition has ceased, and the heat has been raised, being collected apart, and a little oil left in the retort to prevent browning and burning, and the consequent necessity of repeating the entire process from the beginning. (Reichenbach.)

2. *From Beech-tar.* — This substance contains, besides 20 to 25 per cent. of creosote: water, ammonia, hydrocyanic acid, acetic acid, eupione, an oil which turns brown and becomes resinised by exposure to the air, picamar, kapnomor, brown mouldy [and resinous] matters, paraffin, sebacic acid and oleic acid. (Reichenbach.) — *a.* The oily portion of the tar is distilled off in iron retorts, at a heat not sufficient to produce either tumefaction or charring, leaving 40 per cent. of pitch, which should have such a consistence that it is brittle in the cold but plastic at the heat of the hand. The acid watery layer, amounting to 15 p. c. of the two, is then decanted from the heavy oil which has passed over, and if above this watery layer there floats a light oil chiefly consisting of eupione, this is also removed. The lower oil is then

distilled at a gradually increasing heat, the oil which first passes over being set aside as long as it floats upon water; the distillation stopped as soon as the appearance of heavy whitish-yellow vapours indicates the copious evolution of paraffin; and the whole of the oils thus obtained, separated by repeated distillation, with change of receiver, into an oil rich in eupione, which when redistilled to the end, yields a product that floats upon water, and an oil rich in creosote, which from the very beginning yields a product sinking in water. Carbonate of potash is then added to the latter, with heating and agitation, till it no longer causes effervescence, and a small sample of the oil shaken up with water no longer reddens litmus; and the oil, after cooling at rest, is separated from the saline ley containing acetic acid, and rectified, setting aside the first portion of the distillate, in case it floats on water, and taking care not to burn the portions near the sides of the vessel: for this last reason the liquid should not be distilled to perfect dryness. The distillate is then repeatedly treated (as in the preparation from wood-vinegar) with phosphoric acid and water; distilled over phosphoric acid; dissolved in like manner in potash; the solution freed from the eupione which rises to the top, and heated in the air; the creosote separated by sulphuric acid and distilled; and the process repeated, from the treatment with potash onward, just as in the preparation of creosote from wood-vinegar. — (p. 140; from the words: the colourless oil which has passed over is further dissolved, &c. down to: and the consequent necessity of repeating the entire process from the beginning.) — In the distillation of creosote from coal-tar or animal tar, the treatment with carbonate of potash may be dispensed with; but the separation of the ammonia by phosphoric acid requires greater care. (Reichenbach.)

*b.* Tar obtained from hard wood is distilled in a copper still of treble capacity, the portion which first passes over being rejected, and the distillate not collected till a very acid liquid passes over, from which water throws down an oil, and the fire removed as soon as the liquid in the retort begins to decrepitate. The distillate is neutralised with carbonate of potash and distilled with a large quantity of water; the oil which first passes over and floats on water removed; and the distillation continued, the water which passes over being repeatedly poured back into the still till the quantity of the heavy oil no longer undergoes any considerable increase. This heavy oil is dissolved in potash-ley of sp. gr. 1·12; the eupione which rises to the surface taken off; the alkaline liquid, which contains an equal quantity of eupione in solution, distilled with its own volume of water, which must be renewed from time to time, as long as any eupione passes over; a quantity of dilute sulphuric acid equal to $\frac{1}{3}$ of that which is required to neutralise the potash, then introduced into the still; and the distillation continued, whereupon creosote containing eupione is first obtained, and then a small quantity of pure creosote; lastly, the contents of the still are slightly supersaturated with sulphuric acid; and, by further distillation, changing the receiver and pouring back the water, till no more oil distils over, the greater part of the creosote free from eupione is obtained. This pure creosote, together with the creosote-water which passes over with it, is mixed in a still with just sufficient potash-ley to give it a slight alkaline reaction, and rectified, the water being repeatedly poured back as before. Lastly, the creosote, after being mechanically separated from the water, is distilled from a glass retort in the sand-bath, the receiver being changed and the neck of the retort dried as soon as all the water has passed over. Should the creosote thus

obtained turn red on exposure to the air, it must be redistilled in the same manner. (Ed. Simon, *Pogg.* 32, 119.)

*c.* Wood-tar is distilled with a small quantity of sand, and the oil which sinks in water is collected apart. This oil is then mixed in a basin with twice its bulk of water, to which sulphuric acid has been added in sufficient quantity to make the oil float upon it; gradually heated to the boiling point; and kept in a state of ebullition for some minutes. The brown oil, after cooling, is separated from the colourless acid liquid below; rectified; again treated with the above-mentioned acid liquid, whereby it is again turned brown; once more rectified; the pale yellow rectificate dissolved in a quantity of potash-ley not sufficient to dissolve the whole of the creosote; the oil rich in eupione which floats on the top removed; the alkaline solution heated with the above-mentioned acid liquid; the coloured creosote which separates, removed, washed by agitation with water, and rectified after being mixed with sufficient potash to give it an alkaline reaction; the colourless oil mixed with a small quantity of potash-ley and set aside for some weeks in an open bottle placed in a cellar; and the liquid, which has then become brown, carefully rectified. By this method, a large quantity of potash is saved. (Hübschmann; *Ann. Pharm.* 11, 40.)

¶. *d.* The heavy yellow oil distilled from wood-tar by Reichenbach's process (pp. 140, 141) is dissolved in potash-ley; heated to the boiling-point with dilute sulphuric acid; the separated creosote distilled with water; and these operations repeated several times. To purify the creosote thus obtained from certain oils which cause it to turn yellow by keeping, it is dissolved in excess of strong solution of potash; the solution mixed with water, and the separated oil removed; the clear solution boiled for some time in a still, whereupon a colourless oil of nearly the same density as the water passes over with it; and the boiling continued till the milky water likewise containing creosote which passes over, becomes clear on addition of dilute potash. The dark yellow compound of creosote and potash remaining in the still is then mixed with dilute sulphuric acid in such quantity as to leave it slightly alkaline, and distilled, whereupon colourless creosote passes over with the water. The creosote thus obtained began to boil slightly at 100°; and as the boiling point steadily rose, creosote distilled over with the water; between 200° and 208°, the thermometer rose but slowly, and colourless anhydrous creosote then passed over; above 208°, the distillate consisted of creosote having a faint yellow colour; and at 220°, a small quantity of brown-black substance, viscid while warm, solid in the cold, and still containing creosote, remained in the retort. On rectifying the creosote which had passed over between 200° and 208°, the greater part distilled between 200° and 205°, the smaller portion between 205° and 209°; the last portion of the distillate had a yellowish colour, and in this distillation also there remained a small quantity of viscid matter which solidified on cooling. (Völckel, *Ann. Pharm.* 86, 66.) ¶. — A sample of crude creosote prepared from beech-tar by Reichenbach's process began to boil at 90°, the boiling point steadily rising, and by far the largest portion distilling over between 203·5° and 208°. On again rectifying this portion, setting it aside for a day with fused chloride of calcium and rectifying once more, the boiling point remained constant for some time at 203·5 and then slowly rose. (Gorup-Besanez, *Ann. Pharm.* 86, 223.) Gorup-Besanez is of opinion that creosote boiled for some time with strong

potash-ley, as in Völckel's process of purification, undergoes a slow decomposition (see p. 146). ¶.

[Respecting the preparation of creosote, see also Krüger, *Repert.* 47, 273); Buchner (*Repert.* 49, 84); Köne (*Ann. Pharm.* 16, 63); Cozzi (*Repert.* 55, 69.)

3. *From Coal-tar.* — *a. Preparation of Runge's Carbolic acid.* — 12 pts. of the oil obtained by distilling coal-tar with oxide of copper, are mixed with 2 pts. of lime and 50 pts. of water, and the mixture set aside for eight hours and frequently shaken; the brown-yellow watery filtrate thence resulting, boiled down to one-fourth, whereby aniline, leucol and pyrrhol are driven out; the liquid filtered when cold; the impure carbolic acid precipitated from the filtrate by hydrochloric acid in the form of a brown oil; this oil washed with water, after the aqueous liquid has been decanted off; then distilled with water till $\frac{2}{3}$ of the oil has passed over (the brown-black pitchy residue contains rosolic and brunolic acids); the distillate, which is milky at first, but afterwards deposits clear oily drops, mixed with a quantity of water sufficient to dissolve the oil, and precipitated by subacetate of lead; and the curdy precipitate of carbolate of lead, after washing and thorough drying (which is most easily effected after the addition of a small quantity of sulphuric or hydrochloric acid), subjected to dry distillation, whereupon it melts, and gives off carbolic acid (or water at first, if not thoroughly dry,) in the form of a yellow oil, which, by rectifying with a fresh rceiver, may be obtained colourless and free from water. — The easiest method of obtaining a pure product, is at once to distil the carbolic acid contained in the above-mentioned milky distillate, first with water, then with 4 or 5 per cent. of hydrate of potash. (Runge.) — In the distillation of the lead-precipitate, neutral creosote passes over first, and then acid creosote, which, from partial decomposition by heat, contains acetic acid, kapnomor and other products, and is therefore not completely soluble in potash. (Reichenbach, *Pogg.* 31, 497.)

*b. Preparation of Hydrate of Phenyl, according to Laurent.* — Coal-tar is distilled till anthracene begins to pass over; the resulting oil rectified, collecting apart the portion which distils over between 150° and 200°; this portion mixed with saturated potash-ley and pulverised hydrate of potash, whereby it is immediately converted into a white crystalline magma; this substance dissolved in hot water; the oil which rises to the surface removed; the lower alkaline liquid neutralised with hydrochloric acid; the impure hydrate of phenyl, which rises to the surface as an oil, washed with a little water, digested over chloride of calcium, rectified several times, and gradually cooled to — 10° in a closed bottle; and the resulting crystals of pure hydrate of phenyl, freed from the remaining fluid portion by inverting the bottle over another, care being taken to exclude the air, which might give up water to the crystals. (Laurent.) — The tedious fractional distillations involved in this process may be considerably abridged by introducing into the portions which boil between 186° and 188°, a few crystals of pure hydrate of phenyl; a considerable portion of the liquid then solidifies after a while in colourless needles, which, when separated from the liquid, distil at 184° and yield a sublimate of pure hydrate of phenyl. (Williamson & Scrugham, *Chem. Soc. Qu. J.* 7, 237.)

When less carefully prepared, creosote may contain: 1. *Water.* A few drops of the creosote heated in a test-tube a little above 100°, deposit a film of moisture. — 2. *Ammonia.* Water saturated with such creosote

does not remain clear when mixed with neutral acetate of lead, but forms a greasy precipitate soluble in alcohol. — 3. *Acetic* acid may be suspected when the creosote reddens litmus. — 4. *Eupione.* The solution of such creosote in concentrated potash gives up the eupione on dilution with water, the eupione then rising to the top. — 5. *Easily oxidable oil which quickly turns brown.* Creosote thus contaminated turns brown in a day on exposure to the air. Its solution in a treble quantity of strong potash turns brown instead of remaining colourless or assuming merely a faint red tint. Its saturated aqueous solution forms with a drop of ferric sulphate, not a red-brown but a black-brown precipitate. — 6. *Picamar.* Such creosote tastes bitter. A drop of it dissolved in alcohol containing a small quantity of baryta-water forms a white precipitate. It may be purified by twice distilling it with water, till only a small quantity of oil passes over with the water. The picamar being less volatile remains behind. — *Kapnomor*, which deprives the creosote of its corrosive action (*J. pr. Chem.* 1, 18), and a principle of tremendous emetic power (*Pogg.* 29, 62), are also found in badly-prepared creosote. (Reichenbach.)

Pure carbolic acid should impart to fir-wood, on addition of hydrochloric acid, a pure blue colour; a green colour indicates the presence of aniline; a brownish colour that of pyrrhol. — It ought not to turn brown in the air, even after addition of ammonia; and it should produce with ferric sulphate, not a red but a pure lilac colour. (Runge.)

Creosote adulterated with at least 40 per cent. of alcohol, forms a turbid mixture when shaken up with six times its volume of almond-oil at 20° to 30°; alcohol likewise diminishes its specific gravity. (Lepage, *J. Chim. med.* 23, 491.)

*Properties.* Ph. (hydrate of phenyl) crystallises at ordinary temperatures in long colourless needles, belonging to the right prismatic system, sp. gr. 1·065 at 18°; (1·0627 according to Scrugham); melts at 34° to 35°; boils at 187° to 188° (at 184° according to Scrugham); smells very much like creosote, attacks the skin like that substance, and does not redden litmus. (Laurent.)—Carb. (Runge's carbolic acid) is a colourless oil of sp. gr. 1·062 at 20°; refracts light strongly; crystallises under certain circumstances [when more completely dried ?] in long needles which do not melt till heated above 15°; boils at 197·5°; has an empyreumatic odour, like that of castoreum, and a strong, burning, caustic taste. On the skin, it forms brown and white spots, which turn red in a minute, and peel off after a few days. Its aqueous solution causes pain when introduced into the eye or into wounds (in the latter case producing coagulation of albumin, but not stopping the blood); plants immersed in it quickly wither. Neutral. A deal-shaving moistened with its solution in 300 pts. water, and then with hydrochloric or nitric acid, acquires in half-an-hour a beautiful blue colour, which is not destroyed by chloride of lime. (Runge.) — The piece of wood is soaked in aqueous carbonic acid, dipped for a moment into dilute hydrochloric acid, and then exposed to the sun. (Städeler.) Fir-wood, even when simply moistened with hydrochloric acid, often exhibits a blue, violet or green colour on exposure to sunshine. (Wagner, *J. pr. Chem.* 52, 451.) — Kr. (creosote) is a transparent, colourless oil, of sp. gr. 1·037 (1·040, according to Gorup-Besanez, which does not solidify at − 27° [on account of the presence of water ?]; refracts light more strongly than sulphide of carbon. It has the consistence of almond-oil; forms at 20°, drops three times smaller than those of water; makes grease-spots on paper which disappear in a few hours; does not conduct electricity; expands from 100 to 116° vol. when

heated from 20° to 203°; boils at 203° under a pressure of 0·72 met.; distils unchanged and without residue; volatilises completely in a few days when exposed to the air on glass; has a repulsive penetrating odour, at a distance like castoreum, when close, something like smoked meat; its taste is extremely burning and caustic (with sweetish after-taste); it corrodes the tongue, and is perfectly neutral. Kr. smeared on the skin, and washed off after a minute, leaves a spot which looks as if it had been singed, but is neither inflamed nor painful, and after a few days becomes brittle, the cuticle scaling off. In the eye or in wounds, it instantly produces a violent burning pain. Plants are killed by it, and likewise small animals, with convulsions. (Reichenbach.) Even dogs are killed by a few drops of it in a quarter of an hour, with convulsions. (Wöhler & Frerichs, *Ann. Pharm.* 65, 344.)

| | *Hydrate of Phenyl.* | | Laurent, *from Coal-tar.* | Gerhardt, *from Salicylic acid.* |
|---|---|---|---|---|
| 12 C | 72 | 76·59 | 77·13 | 76·04 |
| 6 H | 6 | 6·38 | 6·64 | 6·58 |
| 2 O | 16 | 17·03 | 16·23 | 17·38 |
| $C^{12}H^6O^2$ | 94 | 100·00 | 100·00 | 100·00 |

*Creosote.*

| | Ettling. | | Gorup-Besanez (*mean of* 8 *analyses.*) | Deville. | | | Völckel. |
|---|---|---|---|---|---|---|---|
| C | 75·72 | 74·53 | 75·21 | 72·30 | 72·54 | 72·92 | 72·45 |
| H | 7·80 | 7·87 | 7·92 | 7·60 | 7·60 | 8·16 | 7·10 |
| O | 16·48 | 17·60 | 16·87 | 20·10 | 19·86 | 18·92 | 20·45 |
| | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 |

In Reichenbach's creosote analysed by Ettling, Liebig (*Ann. Pharm.* 6, 209) suggests with reason that there was still water present.—¶. Gorup-Besanez deduced from his analyses above-quoted the formula $C^{26}H^{15}O^4$ which requires 76·47 C and 7·84 H. Völckel regarded the creosote analysed by Gorup as impure, and attempted to purify his own by boiling with dilute potash (see page 142). For the creosote thus purified he deduced from his analyses the formula $C^{24}H^{14}O^5$, which requires 72·72 C and 7·07H.—On the other hand, Gorup, in a subsequent memoir (*Ann. Pharm.* 96, 39), states that creosote is gradually decomposed by boiling with potash. By dissolving creosote in strong potash-ley, boiling the solution for 5 hours on 7 successive days, till the milky liquid which distilled became clear on addition of dilute-potash (p. 142), then distilling the residue with sulphuric acid, and rectifying, a colourless creosote was obtained having the sp. gr. 1·057 at 13°, boiling between 202° and 210°, and dissolving completely in dilute potash and in acetic acid (a character which Völckel considers as essential to pure creosote). It gave by analysis 74·76 to 74·98 C and 7·78 to 7·84 H, numbers corresponding pretty nearly with the formula $C^{24}H^{25}O^4$, which requires 75·39 C and 7·85 H. On redissolving this creosote in potash, boiling the solution for five hours on four successive days, and separating the creosote from the residue as before, the amount of carbon was found to be diminished, analysis giving 73·53 p.c. C and 7·68 H; and by again boiling this creosote with potash and separating as before, a small quantity of distillate was obtained,

which gave 73·43 and 73·72 p.c. C, and 7·72 and 7·71 p.c. H, numbers agreeing pretty nearly with the formula $C^{24}H^{14\cdot5}O^{4\cdot5}$, which requires 74·03 C and 7·45 H. The quantity of creosote was diminished at each boiling with potash, so that a pound was ultimately reduced to a few grammes; and moreover in each case the liquid which distilled over at a certain time from the commencement of the boiling, gradually acquired by exposure to the air a purple-violet colour, the production of which was accelerated by addition of potash; but after the boiling had been continued for a still longer time, the distillate remained colourless on exposure to the air, even after addition of potash. These phenomena are regarded by Gorup as indicative of gradual decomposition, which he supposes to consist in the substitution of oxygen for hydrogen. The potash with which the creosote had been boiled, always gave off carbonic acid on addition of sulphuric acid. — Deville's analyses (quoted by Gerhardt, *Traité de Chim. org.* 3, 20) are extracted from a paper published by that chemist in 1843; the third of these analyses was made with creosote prepared by Reichenbach himself; the other two with products prepared by Pelletier. The results of these analyses differ considerably from those of Ettling and Gorup, and do not agree very well with the formula subsequently given by Deville, viz. $C^{28}H^{16}O^4$; but they agree very nearly with those obtained by Völckel. — Williamson, from experiments made by Fairlie (*Chem. Soc. Qu. J.* 7, 232) concludes that creosote (from coal-tar) is mainly a mixture of hydrate of phenyl with the homologous substance *hydrate of cresyl* $C^{14}H^8O^2$. Probably the samples of wood-tar creosote analysed by Gorup-Besanez and others were similarly constituted. At all events, the formula $C^{26}H^{16}O^4$ given by Gorup is nearly intermediate between $C^{12}H^6O^2$ and $C^{14}H^8O^2$. ¶.

The radical theory assumes the existence of a radical, *Phenyl* = $C^{12}H^5$, and an *oxide of phenyl* $C^{12}H^5O$, the hydrate of which $C^{12}H^5O,HO$, is carbolic acid. According to this view, carbolic acid should be regarded as an alcohol, whereas it rather exhibits the relations of an acid aldide; and in that character it is represented by the above formula $C^{12}H^6,O^2$, (first assumed by Laurent, *Rev. scientif.* 14, 341), the basis of which is not $C^{12}H^4$, but the actually existing compound $C^{12}H^6$.

*Decompositions.* 1. Kr. may be *set on fire* in a heated spoon or in a wick, and burns without residue, producing a white very smoky flame (Reichenbach); a yellow very smoky flame (Runge); a smoky flame (Laurent). — 2. Kr. does not become coloured by exposure to *air* and sunshine, but assumes a reddish tint when exposed to the air after very long boiling or when mixed with aqueous potash or ammonia (Reichenbach); compare p. 149. — 3. Kr. passed very slowly by drops through a *red-hot porcelain tube*, is resolved into a combustible gas loaded with naphthalin vapour; into crystallised naphthalin, and hard, iron-black, graphite-like, rolled up laminæ of charcoal, which do not burn at a red heat; together with a small quantity of tasteless, greasy soot, containing a substance which dissolves readily in alcohol. (Reichenbach, *comp.* Hofmann, *Ann. Pharm.* 55, 205.)

4. Ph. is converted by *chlorine* into hydrochloric and bichlorocarbolic acids, then into terchlorocarbolic acid; and by bromine, with great evolution of heat, into hydrobromic and terbromocarbolic acids. (Laurent):

$$[C^{12}H^6O^2 + 6Cl = C^{12}H^3Cl^3O^2 + 3HCl].$$

*Chlorine-gas* absorbed by cold Kr. forms hydrochloric acid and a brown

resin; from creosote-water chlorine gas throws down a red oil. When chlorine gas is passed into creosote, the liquid becomes turbid, subsequently giving off hydrochloric acid, and acquiring, first a brownish, then a red purple colour; no definite product appears to be formed. (Gorup-Besanez.) *Bromine* dropped into Kr. forms a rose-coloured mixture, with rise of temperature and a crackling hissing noise; from creosote-water it throws down a yellow-red oil. Alcoholic (but not aqueous) *iodine* precipitates from creosote-water a dark-coloured oil. (Reichenbach.) — Kr. is not perceptibly altered by distillation with an equal weight of iodine. (Guyot, *J. scienc. phys.* 5, 230.)

5. *Chloride of lime* converts Kr. into a resinous body. — 6. Ph. treated with chlorate of potash and strong hydrochloric acid, the action being ultimately assisted by heat, is converted, first into a red-brown, crystalline pasty mixture of chloranil, and a red, viscid, fetid resin, which may be extracted by cold alcohol, and when distilled, melts, forms charcoal, yields a distillate containing a large quantity of hydrochloric acid, and a red solidifying oil consisting of terchlorocarbolic acid, and is finally converted into a light yellow crystalline mass of chloranil. (A. W. Hofmann, *Ann. Pharm.* 52, 57.)

$$C^{12}H^6O^2 + 10Cl + 2O = C^{12}Cl^4O^4 + 6HCl \text{ (Hofmann).}$$

Kr. also yields chloranil (Laurent, *Compt. rend.* 19, 574). — ¶. According to Gorup-Besanez (*Ann. Pharm.* 86, 237), the products of the action of hydrochloric acid and chlorate of potash upon creosote are *Hexachlorxylone* $C^{26}Cl^6H^6O^6$, and in smaller quantity, *Pentachlorxylone* $C^{26}Cl^5H^7O^6$. ¶. — 7. Nitric acid dropped into Ph. produces a rattling hissing noise, and at a boiling heat converts it into picric acid. (Laurent):

$$C^{12}H^6O^2 + 3NO^5 = C^{12}(NO^4)^3H^3O^2 + 3HO.$$

Carb. forms, even with dilute nitric acid, a red-brown mixture, which, when the nitric acid is in excess, deposits a black resin. (Runge.) Kr. treated with strong nitric acid becomes heated, gives off red fumes, with sufficient violence to cause spirting, and acquires a dark brown colour. (Reichenbach.) — Laurent (*Compt. rend.* 19, 574), by boiling Kr. with dilute nitric acid, obtained picric acid, oxalic acid, and a brown resin which, when subsequently treated with ammonia and nitric acid, was resolved into picric acid and two other nitro-acids, which formed yellow, laminæ and needles with ammonia. (*Comp.* Gorup-Besanez, *Ann. Pharm,* 232) — 8. Oil of vitriol dissolves Ph. with slight elevation of temperature and in all proportions, yielding a colourless mixture in which sulphocarbolic acid is formed. (Laurent). — A mixture of Carb. with $\frac{1}{5}$ pt. oil of vitriol is colourless, but assumes a rose-colour at the boiling heat; a mixture with $\frac{1}{2}$ pt. oil of vitriol is pale yellow and becomes yellowish red on boiling; with excess of oil of vitriol, a pale yellow mixture is formed, which, at a boiling heat, gives off sulphurous acid and becomes black-brown. (Runge.) Kr. forms with $\frac{1}{20}$ pt. of common or of fuming oil of vitriol, a rose-coloured mixture, which, on exposure to the air, becomes milky from absorption of water, limpid creosote afterwards separating out. With a larger quantity of oil of vitriol, a purple-red mixture is produced; with a still larger quantity, a black-red transparent mixture, which when boiled gives off sulphuric acid and becomes black and opaque. Oil of vitriol, distilled with excess of Kr. is completely

decomposed, creosote distilling over at first and afterwards sulphur. When Kr. is distilled with excess of oil of vitriol, it is completely decomposed, sulphurous acid being evolved, and the mass frothing up, blackening and solidifying into a carbonaceous mass. (Reichenbach.) — Anhydrous sulphuric acid decomposes Kr. immediately, with deposition of finely-divided charcoal. (A. Vogel, Junr. *J. pr. Chem.* 23, 512.) — Kr. forms with oil of vitriol a purple-red mixture containing a compound which forms a baryta-salt, soluble, but quickly decomposing when the solution is evaporated. (Gorup-Besanez.) — A mixture of sulphuric and nitric acid acts violently on creosote, forming a yellowish-red solution, which, when largely diluted with water, yields a small quantity of whitish-yellow, amorphous, explosive substance. (Gorup-Besanez.)

9. Ph. immersed in aqueous *chromic acid* immediately turns black. (Gerhardt.) — Bichromate of potash added to creosote-water slowly throws down a brown resin. Aqueous manganic acid dropt into Kr. becomes brown, the creosote at the same time turning red. A small quantity of creosote-water added to aqueous manganic acid throws down, a brown oxide; excess of creosote-water forms a yellow precipitate soluble with yellow colour in alcohol. Boiling aqueous *molybdic acid* is converted into brown molybdic oxide, the creosote assuming a yellowish-red colour. (Reichenbach.) — 10. Ph. as well as Kr. dropt upon *peroxide of lead* causes evolution of heat and slight hissing, and on subsequent boiling with water, forms a substance containing protoxide of lead. (Laurent). — No decomposition takes place on boiling Kr. with peroxide of lead or peroxide of manganese. — Kr. quickly reduces *gold* from the dilute hydrochloric acid solution; *silver* is reduced by it from the solution of the nitrate or acetate, slowly in the cold, quickly on boiling. (Reichenbach.) ¶. Kr. heated with nitrate of silver produces a silver speculum; when dropt upon recently-precipitated silver-oxide, it becomes heated so much as to take fire with explosion; when silver-oxide is gradually added to creosote, the liquid assumes a dark colour, silver is reduced, and oxalate of silver formed, together with several resinous compounds. Kr. likewise reduces the salts of other noble metals. (Gorup-Besanez.) ¶. —With bichloride of platinum, it slowly assumes a yellow colour and deposits a brown resin soluble in alcohol. (Reichenbach.) — 11. Ph. boiled with mercuric oxide or nitrate, reduces the mercury to the metallic state. (Laurent.) — Kr. heated with mercuric oxide reduces it to the metallic state, itself becoming red, and afterwards brown and more viscid; if sufficient oxide is present, the Kr. is converted on cooling into a brittle resin. (Reichenbach.) — 12. Creosote-water, added to solution of ferrous sulphate, gradually throws down a red-brown adhesive mixture of resinised creosote and ferrous sulphate. (Reichenbach.)

Ph. may be distilled undecomposed with glacial phosphoric acid. (Laurent.)

13. Ph. in contact with pentachloride of phosphorus, immediately evolves hydrochloric and cholorophosphoric acid and leaves chloride of phenyl in the form of a heavy oil:

$$C^{12}H^6O^2 + PCl^5 = HCl + PCl^3O^2 + C^{12}ClH^5.$$

(Cahours, *Compt. rend.* 22, 486; Gerhardt & Laurent, *Compt. rend.* 28, 173). — ¶. 2 At. pentachloride of phosphorus and 5 At. hydrate of phenyl yield chloride of phenyl, and terbasic phosphate of phenyl, together with chlorophosphoric acid [oxychloride of phosphorus] and hydrochloric acid. (Williamson and Scrugham, *Chem. Soc. Qu. J.* 7, 238.)

[The simplest expression of the foregoing result is given by the equation :

$$5(C^{12}H^5,H,O^2) + 2PCl^5 = 2C^{12}H^5Cl + P(C^{12}H^5)^3O^8 + PCl^3O^2 + 5HCl.$$

The quantity of chloride of phenyl obtained is however much smaller than this equation would indicate, the principal product being the phosphate of phenyl. (W.)] ¶.

14. Ph. as well as Carb. and Kr., in contact with potassium, especially if heated, gradually gives off hydrogen gas and forms needles. (Laurent.) The product of the action is carbonate of potash; if too much heat is applied, inflammation and explosion take place. (Runge.) Kr. with potassium or sodium, gives off hydrogen, especially on application of heat, becoming viscid and turning brown on exposure to the air,

¶. Kr. dissolves in caustic potash, and the solution becomes brownish after standing for a few hours; by continued boiling with potash, the creosote appears to undergo a gradual change, resulting in a diminution of the amount of carbon, and apparently consisting in a gradual substitution of O for H. When Kr. is fused with hydrate of potash or distilled with alcoholic solution of potash, a small quantity of an oily liquid is obtained, colourless at first, but afterwards turning yellow, of strong refracting power, specifically lighter than water, having a pleasant aromatic odour and burning taste, distilling over between 180° and 190°, inflammable, insoluble in water, soluble in alcohol and in ether : this product appears to be identical with Reichenbach's kapnomor. Creosote mixed with lime becomes heated and assumes a blackish colour; on heating the mixture, a milky liquid passes over between 100° and 180°; between 180° and 190° the above-mentioned light oil; and between 203° and 208°, an oil heavier than water, and differing from creosote in odour and in composition. (Gorup-Besanez, *Ann. Pharm.* 86, 223.) According to Völckel on the contrary, (*Ann. Pharm.* 87, 306) pure anhydrous creosote does not become heated by contact with recently ignited lime; on heating the mixture to the boiling point of creosote, that substance distils over unaltered; and it is only when the temperature is raised considerably higher, that the creosote combined with the lime is decomposed, a small quantity of a yellowish oil being given off, and at last a combustible gas. The yellowish oil exhibited a boiling point rising from 120° to above 200°: Völckel regards the least volatile portion of it as identical with kapnomor. ¶.

*Combinations.* With *Water.*

*a. Moist Carbolic acid.* — The crystals of carbonic acid deliquesce in the air to an oil by taking up a trace of water, which makes scarcely any difference in the result of their analysis. (Laurent.) As carbolic acid which is no longer crystallisable contains, according to Gerhardt (*Ann. Pharm.* 45, 25), 74·5 p. c. C, 6·9 H, and 19·6 O, it appears to contain 1 At. water to 3 or 4 At. crystalline carbolic acid ; and it is this small quantity of water that seems to constitute the chief difference between Reichenbach's creosote and Laurent's hydrate of phenyl. It is difficult to dehydrate the oil completely; a lump of chloride of calcium causes it to solidify immediately. (Gerhardt.)

*b. Hydrated Carbolic acid.* — By brisk agitation with not too large a quantity of water at 20°, there is formed, below the aqueous carbolic acid,

an oily layer containing 10 pts. water to 100 pts. Kr. This quantity of water increases with the heat at which the agitation is performed. (Reichenbach.)

c. *Aqueous Carbolic acid; Creosote-water.* — 1 pt. of creosote dissolves at 20° in 80 pts. and at 100° in 22 pts. water, partially separating out from the latter on cooling. (Reichenbach.) Carb. dissolves in 31 pts. water at 20°. (Runge.) The solution exhibits, even to the 10,000th degree of dilution, the burning and afterwards sweetish taste of creosote; and on addition of excess of sulphuric acid, the creosote separates out. (Reichenbach.)

Boiling Kr. dissolves a large quantity of crystallised *boracic acid*, which is deposited as a powder on cooling. (Reichenbach.)

Cold Kr. takes up a small quantity of *phosphorus*, and becomes luminous; when warm, it dissolves a larger quantity, forming a deep yellow solution. (Reichenbach.) The solution forms a black precipitate with nitrate of silver. (A. Vogel, Junr. *J. pr. Chem.* 19, 397.) — Kr. dissolves on agitation in 30 pts. of hot aqueous *phosphoric acid* of sp. gr. 1·135, and forms with another portion of the acid a solution of 1 pt. acid in 30 Kr. Both solutions become turbid on cooling, with partial separation of the dissolved substance. (Reichenbach.)

*Sulphur* dissolves sparingly in cold creosote, but in 2·6 pts. of boiling creosote, which, as it becomes more saturated, assumes a yellow, then a green, and ultimately a brown and red-brown colour, and on cooling, first deposits melted sulphur and then becomes filled with crystals of sulphur. (Reichenbach.) The pale yellow solution of sulphur in boiling carbolic acid, which smells of sulphuretted hydrogen, forms on cooling a solid white crystalline mass. (Runge.) Kr. mixes in all proportions with *sulphide of carbon.* (Reichenbach.) — Kr. dissolves a small quantity of *sulphide of phosphorus*, forming a yellowish fuming liquid, which shines brightly in the dark if exposed to the air. (Böttger.)

Boiling Kr. dissolves a small quantity of *selenium*, which is almost all deposited on cooling. (Reichenbach.)

Cold Kr. dissolves a large quantity of *iodine*, forming a brown-red liquid, which is not decomposed by boiling. (Reichenbach.) Similarly, Runge and Laurent. Cold creosote shaken up with aqueous *hydriodic acid* dissolves a large quantity of it. (Reichenbach.)

Kr. is not more soluble in aqueous *hydrochloric* acid than in water. (Reichenbach.)

Carbolates. Obtained by combining the acid with the pure bases (not with the carbonates.) The carbolates of the alkalis have an alkaline reaction. The salts crystallise partially. A chip of firwood moistened with a solution of one of these salts and then dried, gradually turns blue when moistened with weak hydrochloric or nitric acid. (Runge.)

*Carbolate of Ammonia.* — Carbolic acid absorbs ammoniacal gas abundantly and with evolution of heat, forming carbolate of ammonia. (Laurent; Hoffman, *Ann. Pharm.* 47, 75.) This salt passed in the state of vapour through a glass tube at a low red heat, deposits a small quantity of charcoal, but does not form any aniline, which, however is formed at 300° in sealed tubes, and sparingly when an alcoholic solution of carbolate of ammonia is set aside for a month. (Laurent.) Strong ammonia dissolves quickly in cold creosote, and the mixture turns red when exposed to the air. (Reichenbach.) The salt obtained with Carb. remains colourless, and, even when it contains but little ammonia, exhibits

an alkaline reaction, exhales ammonia, and volatilises. (Runge.) Kr. dissolves in ammonia, even in the cold; and the solution gives off all its ammonia at 100°. (Gorup-Besanez.)

*Carbolate of Potash.* — 1. Carb. heated with a sufficient quantity of potassium, gives off hydrogen and is almost wholly converted into a crystalline mass of carbolate of potash; with a smaller quantity of potassium, it forms an oil, which deposits needles of the same salt on cooling. (Runge, Laurent.) — 2. The liquid formed by heating carb. with hydrate of potash solidifies in the cold to a pulpy mass of needles. (Runge, Laurent.) Kr. in contact with [excess of ?] hydrate of potash becomes heated and forms an upper oily layer of creosote-potash, and below it, an aqueous solution of potash containing a small quantity of creosote-potash in solution. In both layers there are formed nacreous laminæ of creosote-potash, which rises to the surface as an oil when the liquid is heated, the laminæ reappearing as it cools. When the Kr. and the hydrate of potash are in right proportion, the entire oily layer crystallises, and numerous crystals float even in the watery layer. In potash-ley of sp. gr. 1·36. Kr. dissolves with evolution of heat, without separation of an oily layer or of crystals. (Reichenbach.) Colourless needles (Laurent, Runge), which, according to their mode of preparation (1), must be $C^{12}H^5KO^2$. (Laurent.) Their solution does not exhibit the corrosive action of free carbolic acid. (Runge.) When subjected to dry distillation, they gave off a large quantity of carbolic acid undecomposed. (Runge.) So likewise their aqueous solution, even when mixed with a large quantity of potash, gives off, when boiled down to a considerable degree of concentration, a large quantity of creosote with the watery vapours. (Reichenbach.) The more concentrated solution becomes red and afterwards brown-yellow by exposure to the air, even in the cold; a more dilute solution, only when heated. (Reichenbach.) Acids separate the carbolic acid from the salt, this effect being produced even by the carbonic acid in the air acting upon the solution. (Reichenbach.) The crystals deliquesce on exposure to the air (Reichenbach), and dissolve very readily in water, alcohol, and ether. (Laurent.)

Dry carbolic acid dissolves dry carbonate of potash, without eliminating carbonic acid, even with the aid of heat. (Runge.)

*Carbolate of Soda.* — 1. Kr. in contact with sodium evolves hydrogen, and forms an oil which does not crystallise by itself, but, if covered with a thin layer of water, forms crystals at the surface of contact. — 2. Kr. mixed with a very strong solution of soda, becomes heated and forms a thin solution which on cooling solidifies into a soapy mass of indistinct crystals. These crystals melt to an oil when heated. They dissolve very readily in water, are insoluble in soda-ley, but dissolve in creosote, forming a thick mass. (Reichenbach.)

*Carbolate of Baryta.* —1. Baryta-water boiled with Ph. till the excess of the latter is expelled, and then left to evaporate in vacuo at ordinary temperatures, yields a crystalline crust, containing 42·48 p. c. baryta, and therefore probably consisting of $C^{12}H^5BaO^2 + 3\ Aq\ [2\ Aq]$. This salt yields by dry distillation, first water, and then a colourless oil which has a sweet and burning taste and contains carbolic acid. (Laurent.)

*Carbolate of Lime.*— Carb. forms with thick milk of lime, a thin syrup which dissolves readily in a larger quantity of water, forming a clear thin liquid, just like that which is formed immediately with thin milk of lime. This liquid, after being mixed with as much milk of lime

as will dissolve in it, contains 48·35 pts. [3 At.?] lime to 100 pts. [2 At.] of the dry acid. A large quantity of alcohol added to it, throws down white crystalline grains soluble in water. By continued boiling, it gives off carbolic acid, and deposits, together with carbonate of lime, a salt containing excess of base, while the liquid, as it cools, deposits a more neutral salt in beautiful crystals. Carbonic acid throws down nearly all the lime from the milk of lime solution. (Runge.)

*Carbolate of Lead.—a. Sesquibasic.* Subacetate of lead is poured into aqueous carbolic acid, which must remain in excess, and the precipitate, which resembles chloride of silver, washed and dried. The white powder becomes yellowish at 138°, cakes together and melts at 200° into a greyish black mass, which contains 65·08 p. c. lead-oxide (3 At. oxide to 2 At. acid); and at a higher temperature, boils up, leaves a black residue, and gives off carbolic acid, colourless and neutral at first, afterwards yellow and reddening litmus. (Runge.)—¶. (Völckel, *Ann. Pharm.* 86, 97; and Gorup-Besanez, *Ann. Pharm.* 96, 54) obtained a similar compound by adding a dilute and slightly ammoniacal solution of neutral acetate of lead to a solution of creosote in absolute alcohol, previously mixed with strong ammonia and diluted with a large quantity of water. Völckel's salt contained (mean) 27·34 p. c. C, 2·52 H, and 63·79 PbO, whence Völckel deduces the formula, $PbO,C^{24}H^{13}O^4 + 2PbO$. Gorup obtained 64·52 p. c. PbO, and gives for his lead-salt the formula, $PbO,C^{24}H^{14}O^3 + 2PbO$. Both these formulæ are highly improbable, Gorup however observes that the first portions of the precipitate obtained by fractional precipitation contained less oxide of lead than the latter portions; and moreover that such lead-compounds are for the most part variable in composition and very apt to decompose. The creosote used by Gorup in the preparation of his lead-compound had been boiled for 7 days, 5 hours each, with strong solution of potash (see p. 145). ¶.

*b. Neutral?*—When subacetate of lead is added to alcoholic carbolic acid, only so long as the precipitate redissolves on agitation, the solution left to evaporate, and the watery liquid, which contains acetate of lead, decanted, there remains a transparent colourless oil, consisting of neutral carbolate of lead, which dissolves clearly in alcohol, but is resolved by water into a precipitate of basic salt, and aqueous carbolic acid containing a small quantity of lead-oxide. The salt *a* likewise dissolves in anhydrous carbolic acid, forming a syrup, which dries up to a varnish on exposure to the air, dissolves in alcohol, but deposits a basic salt when treated with water. (Runge.)

Lead-oxide forms with boiling Ph. a very thick liquid, which, on addition of a single drop of alcohol, solidifies into a white mass somewhat soluble in boiling alcohol. (Laurent.)

Carb. colours *ferric sulphate* lilac and forms a yellow precipitate, (Runge.) Kr. has no visible effect on solution of ferric chloride. (Gorup-Besanez.) Kr. imparts a blue colour to very dilute solutions of ferric salts. (Deville.) — *Cupric hydrate* heated with Kr., first gives off its water, and then dissolves forming a brown solution. *Cupric acetate* dissolves sparingly in cold, more readily in hot Kr. forming a brown liquid, from which an excess of the copper-salt throws down all the oxide, the acetic acid taking up the whole of the creosote. — *Corrosive sublimate* disolves abundantly and without decomposition in boiling Kr., separating out for the most part on cooling. (Reichenbach.) Nitrate of silver dissolves abundantly in cold Kr., but the limpid solution assumes a violet

colour between 30° and 40°, and at a boiling heat, deposits all the silver in the metallic state. (Reichenbach.) Concentrated *chloride of gold* mixes undecomposed with cold creosote. (Reichenbach.)

Carbolic acid mixes in all proportions with *alcohol* and *ether*. (Reichenbach, Runge, Laurent.) Similarly with *acetic ether*. (Reichenbach.) A few drops of alcohol or ether are sufficient to prevent the crystallisation at ordinary temperatures. (Laurent.) The solution of 1 vol. Kr. in 10 vol. absolute alcohol is rendered turbid at 20° by the addition of 12 vol. but not of 11 vol. water. (Reichenbach.)

Kr. mixes in all proportions with *acetic acid* of sp. gr. 1·070 (also Ph. with strong acetic acid: *Laurent*), and dissolves in the dilute acid much more abundantly than in water. It dissolves in 17 pts. of a cold, and in 10 pts. of a warm mixture of equal pts. of glacial acetic acid and water. Its solution in 20 pts. of the strong acid is not clouded by water; from a solution in very dilute acetic acid, the creosote is separated by Glauber's salt. (Reichenbach.) It dissolves a large quantity of *acetate of ammonia;* also at a boiling heat, large quantities of the *acetates* of *potash*, *soda* and *zinc*, which crystallise out on cooling; and *acetate of lead* (which dissolves even in the cold) so abundantly, that the solution on cooling, solidifies into a mass composed of needles. (The acetates of baryta, strontia, and lime do not dissolve in creosote). (Reichenbach.)

The solution of crystallised *oxalic, tartaric* or *racemic* acid in boiling creosote, solidifies in the crystalline state on cooling. *Succinate of ammonia* dissolves in boiling creosote. Uric acid does not dissolve in it (Reichenbach.)

Creosote dissolves picric, benzoic, citric, oleic, margaric, and stearic acids; mixes with volatile oils; dissolves naphthalin, common camphor, stearin, spermaceti, cholesterin, cerin, myricin, and paraffin, many resins, indigo and many other colouring matters, and many alkaloids; it coagulates albumen; precipitates a concentrated solution of gelatin (*Runge*); and prevents or retards the putrefaction of animal substances. (Reichenbach.)

### *Appendix to Carbolic Acid.*

## 1. Rosolic Acid.

RUNGE. (1834.) *Pogg*, 31, 70.

Formed from an unknown substance contained in coal-tar, on heating that body with alkalis. When the tar is shaken up with milk of lime, and the colourless or yellowish filtrate boiled for some hours, it assumes a dark red colour, and, after a few hours, deposits a dark red powder consisting of rosolate of lime.

*Preparation*. The brown-black pitch (p. 142) containing rosolic and brunolic acid, which remains to the amount of one-third in the distillation of impure carbolic acid with water, is boiled with water as long as carbolic acid continues to volatilise; then dissolved in a small quantity of alcohol; milk of lime added; the rose-coloured solution of rosolate of

lime filtered from the precipitated brunolate of lime; the rosolic acid, still containing brunolic acid, precipitated therefrom by acetic acid; and this precipitate treated in like manner with alcohol, lime, and acetic acid, as long as the lime produces any precipitate of brunolate of lime. The rosolic acid precipitated by the acetic acid is then collected on a filter, dissolved in alcohol after washing and drying, and the alcohol left to evaporate.

Yellowish-red, pulverisable resin.

*Rosolate of lime* separates from its aqueous solution evaporated to a syrup, on the addition of $\frac{1}{3}$ pt. alcohol, in deep red crystals.

Rosolic acid forms with appropriate mordants, beautiful red lakes and coloured tissues. (Runge.)

By supersaturating with hydrochloric acid the precipitate of brunolate of lime obtained in the purification of rosolate of lime, and repeatedly treating the brunolic acid which falls down in brown flakes, with lime and hydrochloric acid, to remove all the rosolic acid, then dissolving in soda, precipitating from the filtrate by hydrochloric acid, and evaporating the alcoholic solution, pure *Brunolic acid* is obtained. (Runge.)

## 2. Taurylic Acid.

$$C^{14}H^8O^2 = C^{14}H^8,O^2.$$

STÄDELER. *Ann. Pharm.* 77, 17.

*Taurylic acid.* Carbolic acid occurs in the urine of cows, horses, and man, together with taurylic acid, which appears to contain $C^2H^2$ more, and therefore to be $C^{14}H^8O^2$, but has not yet been completely separated. To obtain the mixture of the two acids, cow's urine is boiled with lime; the decanted liquid evaporated to one-third, supersaturated when cold with hydrochloric acid, separated after 24 hours from the crystallised hippuric acid, and distilled; the distillate, which is clouded with greenish and yellowish drops of viscid oil having an offensive odour, distilled with excess of potash, (whereupon a neutral azotised oil, heavier than water and smelling like rosemary, passes over together with a little ammonia); the residue mixed with a quantity of sulphuric acid sufficient to neutralise only $\frac{5}{6}$ of the potash (so that no hydrochloric or benzoic acid may be given off); the liquid distilled as long as that which passes over precipitates basic acetate of lead; the distillate, which smells exactly like carbolic acid, repeatedly rectified over common salt, till only a small quantity of watery liquid is found mixed with the oily distillate; these two liquids repeatedly shaken up together for twelve hours with carbonate of soda (to remove damaluric and damolic acid, which impart a strong acid reaction); the oil, which remains in diminished quantity, extracted from the mixture by ether; the ether distilled off; the oily residue distilled with strong potash-ley (whereupon a small additional quantity of neutral oil passes over); the residue distilled with bichromate of potash; and the oil which distils over, set aside for some time in contact with chloride of calcium, and distilled therefrom, with frequent change

of receiver. It then begins to distil at 170°, at which temperature water still passes over together with the oil; at 180°, oil is obtained still retaining water in solution; from that point to 195° the largest and purest portion of oil; and at 200°, brownish oil. (Städeler.)

The mixture of carbolic and taurylic acid obtained between 180° and 195° is a colourless oil which does not solidify at − 18°; boils at a somewhat higher temperature than carbolic acid; smells exactly like castoreum; makes a white spot on the skin and then causes desquamation; turns firwood blue on addition of hydrochloric acid; and when added to solution of ferric chloride, first turns it blue and then produces a light-coloured precipitate. Its mixture with an equal volume of oil of vitriol solidifies into an arborescent mass, the mother-liquor of which contains carbolic acid. When boiled with nitric acid, it yields a large quantity of picric acid. (Städeler.)

| | | | Städeler, *Taurylic acid,* at 180°. | 180°—195°. | at 195°. |
|---|---|---|---|---|---|
| 14 C | 84 | 77·78 | 74·90 | 77·1 | 77·14 |
| 8 H | 8 | 7·41 | 7·51 | 7·4 | 7·56 |
| 2 O | 16 | 14·81 | 17·59 | 15·5 | 14·67 |
| N | | | | | 0·63 |
| $C^{14}H^8O^2$ | 108 | 100·00 | 100·00 | 100·0 | 100·00 |

The nitrogen in Städeler's analysis arises from admixture of the neutral oil above-mentioned.

This compound is isomeric with hydrate of cresyl (p. 146).

### *Conjugated Compounds of the Primary Nucleus* $C^{12}H^6$.

## Sulphobenzolic Acid.

$C^{12}H^6S^2O^6 = C^{12}H^6,2SO^3$.

MITSCHERLICH. (1834.) *Pogg.* 31, 283 and 634.

*Sulphophenylic acid, Phenylschwefelsäure, Benzosulphuric acid, Benzinschwefelsäure, Benzidunterschwefelsäure, Funeschwefelsäure, Acide benzosulfurique.*

*Formation.* From benzene and anhydrous sulphuric acid or fuming oil of vitriol, (p. 138).

*Preparation.* Benzene is added, with agitation and frequent cooling, to fuming oil of vitriol contained in a bottle, as long as it dissolves; the solution diluted with water, filtered from the sulphobenzene, and saturated with carbonate of baryta; the filtrate precipitated by the exact amount of cupric sulphate required (because the copper-salt crystallises better than the barium-salt); the filtrate evaporated till it begins to crystallise; the crystals collected after cooling, decomposed by sulphuretted hydrogen; and the filtrate evaporated to a syrup, and cooled.

*Properties.* Crystalline mass.

*Combinations.* The acid dissolves in *water*.

The *Sulphobenzolates* require a strong heat to decompose them. When boiled with excess of a fixed alkali, they are not merely resolved into benzene and a sulphate of the alkali, but likewise yield other products.

The sulphobenzolates of *ammonia, potash, soda, ferrous oxide, zinc-oxide* and *silver-oxide* crystallise very well.

*Baryta-salt.* — Crystalline crusts; (Mitscherlich); white crystalline powder, appearing under the microscope to consist of four-sided rhombic tables. (Gericke, *Ann. Pharm.* c, 208.)

| | | | Buckton & Hofmann. | Gericke. |
|---|---|---|---|---|
| 12 C | 72·0 | 31·92 | | |
| 5 H | 5·0 | 2·21 | | |
| Ba | 68·6 | 30·41 | 30·38 | 30·36 |
| 2 S | 32·0 | 14·18 | 14·19 | |
| 6 O | 48·0 | 21·28 | | |
| $C^{12}H^5Ba,2SO^3$ | 225·6 | 100·00 | | |

The *copper-salt* forms large crystals, which give off all their water at 170°, and do not suffer any further decomposition even at 220°. (Mitscherlich.)

| *Dried at* 180°. | | | Mitscherlich. |
|---|---|---|---|
| 12 C | 72 | 38·10 | 38·28 |
| 5 H | 5 | 2·64 | 2·64 |
| Cu | 32 | 16·93 | 16·44 |
| 2 S | 32 | 16·93 | 16·83 |
| 6 O | 48 | 25·40 | |
| $C^{12}H^5Cu,2SO^3$ | 189 | 100·00 | |

*Sulphobenzolate of Ethyl* $C^{12}H^5(C^4H^5),S^2O^6$.— Formed by heating the lead-salt with iodide of ethyl to 100° in a sealed tube. From an alcoholic solution evaporated over oil of vitriol, it crystallises in slender needles which are not volatile. Heated with potash, it is resolved into alcohol and sulphobenzolic acid; also when the aqueous solution is rapidly concentrated by evaporation. Dissolves readily in water, less readily in alcohol. (Gericke, *Ann. Pharm.* C, 216.)

## ¶. Bisulphobenzolic Acid.

$$C^{12}H^6S^4O^{12} = C^{12}H^6,4SO^3.$$

Buckton & Hofmann. *Phil. Trans.* 1856; abstr. *Chem. Soc. Qu. J.* 9; *Proc. Roy. Soc.* 8, 158.

*Formation and Preparation.* 1. By the action of sulphuric acid upon benzonitrile, sulphobenzoic acid being produced at the same time:

$$C^{14}H^5N + 6HSO^4 = C^{12}H^6S^4O^{12} + H(NH^4),2SO^4 + 2CO^2;$$

and:

$$C^{14}H^5N + 4HSO^4 + 2HO = C^{14}H^6S^2O^{10} + H(NH^4),2SO^4.$$

The action is not attended with great evolution of heat; and no gas is evolved till the temperature is very considerably raised, whereupon benzoic acid sublimes in the neck of the retort, carbon is deposited, and sulphurous acid evolved. The action was continued for some time after the appearance of the sulphurous acid, in order to decompose the sulphobenzoic acid as much as possible; on cooling, a semi-transparent, hard mass having a glassy fracture remained in the retort. This mass boiled with water and carbonate of baryta, evolved ammonia and yielded a mixture of sulphobenzoate and bisulphobenzolate of baryta. The dark-coloured filtrate was then again decomposed by sulphuric acid, boiled with excess of oxide of lead, filtered, and the filtered liquid treated with sulphuretted hydrogen. The greater portion of the colouring matter was carried down with the sulphide of lead; and on saturating the acid liquor with carbonate of baryta, evaporating nearly to dryness, redissolving in water, and adding alcohol, a precipitate was obtained consisting of disulphobenzolate of baryta, mixed however with sulphobenzoate, the greater portion of the latter salt remaining in solution.—2. By the action of fuming sulphuric acid upon sulphobenzolic acid. The latter acid (obtained from the lead or copper-salt) is dried on the sand-bath till it emits white fumes, and exhibits a slight brown colour, indicating incipient decomposition. It is then introduced into a dry retort together with an equal volume of strong Nordhausen sulphuric acid, and the mixture heated to the boiling point for two hours. The liquid is then evaporated to nearly the original bulk of the sulphobenzolic acid used, and the resulting bisulphobenzolic acid decolorised by treating it with oxide of lead, and decomposing the filtrate with sulphuretted hydrogen. On saturating the colourless acid thus obtained with carbonate of baryta, and evaporating, an apparently amorphous baryta-salt is obtained, which however under the microscope, appears distinctly crystalline, exhibiting minute shuttle-shaped forms, which are generally densely grouped together. This salt is very stable, but when strongly heated on platinum foil, it burns and gives off sulphurous acid.

| | | | Buckton & Hofmann, (1) at 170°. | (2) at 195°. |
|---|---|---|---|---|
| 12 C | 72 | 13·30 | | |
| 4 H | 4 | 1·07 | | |
| 2 Ba | 137 | 36·72 | 37·70 | 36·43 |
| 4 S | 64 | 17·16 | | 17·35 |
| 12 O | 96 | 25·75 | | |
| $C^{12}H^4Ba^2S^4O^{12}$ | 373 | 100·00 | | |

The salt (1) still contained sulphobenzoate of baryta, although it had been partially purified by reprecipitation with alcohol. (Buckton & Hofmann.) ¶.

## Sulphophenic Acid.

$$C^{12}H^6S^2O^8 = C^{12}H^6O^2,2SO^3.$$

LAURENT. (1841.) *N. Ann. Chim. Phys.* 3, 203; also *J. pr. Chem.* 25, 408.

*Carbolschwefelsäure, Sulfophanissäure, Acide sulfophenique.*

*Formation and Preparation.* The mixture of carbolic acid with excess of oil of vitriol (p. 147), is mixed with water after standing for 24 hours, and saturated at the boiling heat with carbonate of baryta; the filtrate evaporated to the crystallising point, the crystals purified by recrystallisation from boiling alcohol; the needles of sulphophenate of baryta collected on a filter, washed with a small quantity of alcohol, and decomposed by an equivalent quantity of dilute sulphuric acid; and the filtrate evaporated in vacuo.

By saturating the acid with ammonia, the *ammonia-salt* is obtained in small scales which contain 39·74 p. c. sulphuric acid, and are therefore $C^{12}H^5(NH^4)O^2,2SO^3 + Aq$. When boiled with nitric acid, they yield picric acid in large quantity.

The needles of the *baryta-salt* lose 9·1 p. c. (3 At.) water at 200° in vacuo; give off carbolic acid by dry distillation; and at a red heat leave 42·43 p. c. sulphate of baryta; whence they are $= C^{12}H^5BaO^2,2SO^3 + 3 Aq$. [or 4 Aq. ?] (Laurent.)

### *Oxygen-nucleus* $C^{12}H^4O^2$.

## Kinone. $C^{12}H^4O^4 = C^{12}H^4O^2,O^2$.

WOSKRESSENSKY. (1838.) *Ann. Pharm.* 27, 268; *J. pr. Chem.* 18, 419; 34, 251.
WÖHLER. *Ann. Pharm.* 51, 148.

***Chinon, Chinoyl, Quinone, Quinoïle.***

*Formation.* 1. Sublimes when the salts of kinic acid are burnt at a gentle heat.— 2. More abundantly when kinic acid is heated with manganese and sulphuric acid. (Woskressensky) — ¶. In a similar manner also from caffeic acid, and therefore from the leaves and beans of the coffee plant, the leaves yielding the greater product; also under similar circumstances from the peculiar acid of Paraguay tea; from the leaves of the common holly (*Ilex aquifolium*); the leaves and branches of privet (*Ligustrum vulgare*); from ivy; from the evergreen oak (*Quercus ilex*), the common oak (*Quercus robur*); the common small-leaved elm (*Ulmus campestris*), the ash (*Fraxinus excelsior*), and the *Cyclopia latifolia*, a leguminous plant from the Cape of Good Hope. It was only however from the leaves and berries of the coffee-plant and from the holly that the kinone was obtained in crystals; in the other cases, its formation was concluded from the deep yellow colour of the distillate which passed over at a comparatively low temperature, and from the dark humus-like colouring produced in that distillate by ammonia. No kinone was obtained from the laburnum, from tobacco, from the sloe (*Prunus spinosa*), and from many other plants not specified. (Stenhouse, *Phil. Mag. J.* [4] 7, 21; *Ann. Pharm.* 89, 244.) ¶.

*Preparation.* 1 pt. of kinic acid [or coffee: *Stenhouse*] is distilled with 4 pts. peroxide of manganese, 1 pt. oil of vitriol and ½ pt. water,

whereupon the mixture froths up and gives off dense vapours which condense in the cooled receiver in golden yellow needles; and these crystals are purified by pressure between paper and repeated sublimation. (Woskressensky.) The proportions just given must be strictly observed; if the mixture is too thin, it froths over. Instead of kinic acid, kinate of lime may be used, even the syrupy salt obtained from quinine manufactories. If more than 100 grammes of kinic acid are operated upon at once, the mixture becomes too hot, so that, in spite of the best condensation, a large portion of the kinone is carried away by the hot carbonic acid. If a very capacious flask is used, fitted with a tube 8 ft. long which leads into a well-cooled receiver, and the fire removed as soon as the action begins, the mass becomes sufficiently heated to ensure the continuance of the action, and the greater part of the kinone is deposited in needles in the tube. These needles are rinsed out of the tube with the watery distillate in the receiver, which contains kinone and formic acid; washed several times on the filter with cold water; then pressed; and dried over chloride of calcium within a bell-jar. (The distillate is well adapted for the preparation of green hydrokinone, which may be obtained by mixing it with a quantity of sulphurous acid not sufficient to decompose it completely.) (Wöhler.)

*Properties.* When sublimed, it forms transparent, gold-yellow, long, shining needles (Woskressensky); after crystallisation from hot water, it is darker, of a dingier yellow colour, and less transparent. (Wöhler.) Heavier than water; melts at 100° to a yellow liquid (Woskressensky), which crystallises on cooling. (Wöhler.) Volatilises without alteration (Woskressensky), and sublimes, even at ordinary temperatures, from one part of the containing vessel to another. (Wöhler.) Has a pungent and persistently irritating, tear-exciting odour. (Woskressensky, Wöhler.) A gramme of it taken internally has no effect upon dogs. (Wöhler & Ferricks, *Ann. Pharm.* 65, 343.) The aqueous solution imparts to the skin (by decomposition) a brown colour which cannot be removed by washing. (Wöhler.) Neutral to vegetable colours.

| | | | Woskressensky. | Wöhler. | Laurent. |
|---|---|---|---|---|---|
| 12 C | 72 | 66·67 | 67·31 | 67·37 | 66·4 |
| 4 H | 4 | 3·70 | 3·79 | 3·70 | 3·7 |
| 4 O | 32 | 29·63 | 28·90 | 28·93 | 29·9 |
| $C^{12}H^4O^2,O^2$ | 108 | 100·00 | 100·00 | 100·00 | 100·0 |

Compare Laurent (*Compt. rend.* 21,419, and *Compt. Chim.* 1849, 190); Wöhler (*Ann. Pharm.* 65, 349).

*Decompositions.* 1. The aqueous solution of kinone acquires by exposure to the air, a continually deeper yellowish red colour, and ultimately deposits a black-brown mouldy substance. (Wöhler.) The aqueous solution mixed with ammonia or potash absorbs oxygen and assumes a black-brown colour on exposure to the air, and then forms with acids a black mouldy precipitate, very sparingly soluble in water and alcohol (Woskressensky); doubtless consisting of melanic acid: $C^{12}H^4O^4 + 2O = C^{12}H^4O^6$. (Laurent, *Compt. rend.* 26, 35.) — 2. With dry chlorine gas, kinone forms terchlorokinone, the action being attended

with great rise of temperature and evolution of hydrochloric acid. (Woskressensky):

$$C^{12}H^4O^4 + 6Cl = C^{12}Cl^3HO^4 + 3HCl.$$

3. Heated with hydrochloric acid and chlorate of potash, it is quickly converted into chloranil. (Hofmann, *Ann. Pharm.* 62, 65.) — 4. Oil of vitriol carbonises kinone. (Woskressensky.)—5. Strong hydrochloric acid colours kinone brownish black, and then dissolves it, forming a red-brown, afterwards colourless liquid, which no longer smells of kinone, but contains chlorhydrokinone $C^{12}ClH^5O^4$. (Wöhler.) [The first products are probably kinhydrone and chlorkinhydrone, the presence of both of which in the black magma formed at the beginning of the action, was pointed out by Städeler. (*Ann. Pharm.* 69, 308):

$$4C^{12}H^4O^4 + 2HCl = C^{24}H^{10}O^8 + C^{24}Cl^2H^8O^8;$$

and these compounds, by the further action of the hydrochloric acid, are converted into chlorhydrokinone, being at the same time dissolved and decolorised:

$$C^{24}H^{10}O^8 + C^{24}Cl^2H^8O^8 + 2HCl = 4C^{12}ClH^5O^4].$$

Städeler gives a different explanation of the process.—Chlorhydrokinone is likewise formed by the action of hydrochloric acid gas upon dry kinone. (Wöhler.) — 6. Ammoniacal gas passed over kinone, quickly converts it, with separation of water, into emerald-green crystalline *kinonamide*, which forms with water a nearly black, quickly decomposing solution, and contains 63·06 p. c. C and 4·96 H, and is therefore perhaps $C^{12}NH^6O^3$ [or $C^{12}NH^5O^2$] (Woskressensky: *comp.* Gerhardt, *Compt. Chim.* 1845, 191.) — 7. Sulphuretted hydrogen gas has no action upon dry kinone, but when passed through the cold aqueous solution, first reddens it, and then throws down brown flakes of brown sulphohydrokinone, which, if the passage of the gas be still continued, and especially if the action be aided by heat, is converted into yellow sulphohydrokinone. The same compound is formed when bihydrosulphate of ammonia is poured upon kinone. (Wöhler.) — 8. Kinone dissolved in water is converted into hydrokinone by excess of hydriodic or hydrotelluric acid, with precipitation of iodine or tellurium, and by sulphurous acid, with formation of sulphuric acid. (Wöhler.) — Dry sulphurous acid gas has no action upon dry kinone; and even phosphuretted hydrogen, arseniuretted hydrogen, and hydrocyanic acid are without action upon it. (Wöhler.)

*Combinations.* Kinone dissolves with some difficulty in *water.* (Woskressensky.)

It dissolves with yellow colour in dilute *hydrochloric* or *nitric acid.* (Woskressensky.)

Its aqueous solution throws down from *basic acetate of lead* a pale yellow jelly, but does not precipitate the neutral salts of lead, copper, or silver. (Woskressensky.)

Kinone dissolves with tolerable facility in *alcohol* and *ether.* (Woskressensky.)

## Hydrokinone.

$C^{12}H^6O^4 = C^{12}H^4O^2,H^2O^2$.

WÖHLER. *Ann. Pharm.* 45, 354; 51, 150.

*Colourless Hydrokinone, farbloses Hydrochinon, Hydroquinone incolore.*

*Formation.* 1. The chief product of the dry distillation of kinic acid. — 2. Formed also by treating kinone with hydriodic acid, hydrotelluric acid, or large quantities of aqueous sulphurous acid, or protochloride of tin.

*Preparation.* 1. The distillate mixed with solid particles, which is obtained by the dry distillation of kinic acid, is filtered from the tar, and again, after cooling, to separate benzoic acid; the yellow, heavy, oily mixture of benzene, carbolic acid and salicylous acid, distilled from the filtrate; the brown residue in the retort evaporated and left to cool till benzoic acid crystallises out; the mother-liquor diluted with water, which makes the liquid milky and separates tar; and the resulting filtrate evaporated till the hydrokinone crystallises out. — 2. Sulphurous acid gas is passed through warm water saturated with kinone, and having kinone also suspended in it, till all the kinone is dissolved, and the liquid appears colourless; the solution then gently evaporated to the crystallising point; and the crystals purified by pressure and recrystallisation. — It is not necessary previously to remove the sulphuric acid by carbonate of baryta. — A saturated aqueous solution of kinone may also be mixed with aqueous hydriodic acid, and the watery liquid, after filtration from the iodine, evaporated to the crystallising point.

*Properties.* Transparent, colourless, six-sided prisms, with oblique terminal faces. Easily fusible, crystallising on cooling. Sublimes when heated, in shining laminæ like benzoic acid. Inodorous; has a sweetish taste; neutral to vegetable colours.

| | | | Schnedermann. |
|---|---|---|---|
| 12 C | 72 | 65·45 | 65·91 |
| 6 H | 6 | 5·46 | 5·53 |
| 4 O | 32 | 29·09 | 28·56 |
| $C^{12}H^4O^2,H^2O^2$ | 110 | 100·00 | 100·00 |

May be regarded as an alcohol.

*Decompositions.* 1. Hydrokinone suddenly heated above the boiling point, is partially decomposed into kinone and green kinhydrone. [What becomes of the excess of hydrogen?] — 2. Chlorine, chromate of potash, sesquichloride of iron, or nitrate of silver, converts hydrokinone dissolved in water into green needles of kinhydrone, with formation of hydrochloric acid, chromic oxide, or protochloride of iron and hydrochloric acid, or with precipitation of silver. — 3. The aqueous solution of hydrokinone imparts a saffron-yellow colour to cupric acetate, and when heated throws down cuprous oxide, kinone volatilising at the same time. — 4. With

ammonia it immediately assumes a brown-red colour, and on subsequent evaporation leaves a brown mouldy mass.

*Combinations.* Hydrokinone dissolves easily in *water,* especially when hot.

*Hydrosulphate of Hydrokinone. — a. Bibasic.*—Sulphuretted hydrogen gas passed through a saturated aqueous solution of hydrokinone at 40°, produces very long colourless prisms.

*b. Sesquibasic.* — When a solution of kinone is saturated in the cold with sulphuretted hydrogen, small shining crystals immediately separate from it, which dissolve when heated (supposing the stream of sulphuretted hydrogen to be kept up), and on cooling separate in transparent colourless rhombohedrons, which resemble those of calcspar, and after pressing between paper, and drying in vacuo, are inodorous and permanent in the air.

| *Crystals a.* | | | Wöhler. |
|---|---|---|---|
| 24 C | 144 | 60·76 | |
| 13 H | 13 | 5·48 | |
| S | 16 | 6·75 | 6·78 |
| 8 O | 64 | 27·01 | |
| $2C^{12}H^{6}O^{4},HS$ | 237 | 100·00 | |

| *Crystals b.* | | | Wöhler. |
|---|---|---|---|
| 36 C | 216 | 59·34 | 58·70 |
| 20 H | 20 | 5·50 | 5·51 |
| 2 S | 32 | 8·79 | 8·86 |
| 12 O | 96 | 26·37 | 26·93 |
| $3C^{12}H^{6}O^{4},2HS$ | 364 | 100·00 | 100·00 |

Both kinds of crystals, when melted *per se,* or moistened in contact with the air, or when their aqueous or alcoholic solution is boiled, give off sulphuretted hydrogen and leave hydrokinone.

*Hydrokinone with Acetate of Lead.* — A solution of hydrokinone in warm, moderately concentrated aqueous acetate of lead, deposits, on cooling, oblique rhombic prisms, which give off 5·23 p. c. (nearly 3 At.) water over oil of vitriol. (Wöhler, *Ann. Pharm.* 69, 299.)

| *Air-dried crystals.* | | | Wöhler. |
|---|---|---|---|
| 20 C | 120 | 25·92 | 26·34 |
| 15 H | 15 | 3·24 | 3·10 |
| 2 PbO | 224 | 48·38 | 47·33 |
| 13 O | 104 | 22·46 | 23·23 |
| $C^{12}H^{6}O^{4},2C^{4}H^{3}PbO^{4} + 3Aq$ | 463 | 100·00 | 100·00 |

The aqueous mixture of kinone and neutral acetate of lead, yields, on gradual addition of ammonia, a pale yellow precipitate, which soon sinks together in the form of a grass-green powder, appearing under the microscope to be composed of translucent spherules. In drying, it turns brown and gives off an odour of kinone.

Hydrokinone dissolves readily in *alcohol* and in *ether.* (Wöhler.)

# Melanic Acid.

$C^{12}H^4O^6 = C^{12}H^4O^2,O^4$.

PIRIA. (1839.) *Ann. Chim. Phys.* 69, 281; also *Ann. Pharm.* 30, 167.
WOSKRESSENSKY. *J. pr. Chem.* 34, 251.
LAURENT. *Compt. rend.* 26, 35.

*Melansäure, Chinonsäure, Acide melanique.*

*Formation.* By the action of the air on kinone, or hydrokinone dissolved in aqueous potash or ammonia (p. 159), or on an aqueous solution of salicylite of potash.

*Preparation.* 1. An aqueous solution of kinone mixed with potash and exposed to the air till it turns black, yields with hydrochloric acid a black mouldy precipitate, which is to be washed and dried. (Woskressensky.) — 2. Moistened salicylite of potash is exposed to the air till it is blackened through and through, and the acetate of potash formed at the same time is dissolved out by water. (Piria.)

*Properties.* Black tasteless powder, resembling lamp-black. (Piria.)

| | | | Piria. | Woskressensky. |
|---|---|---|---|---|
| 12 C | 72 | 58·06 | 57·24 | 56·65 |
| 4 H | 4 | 3·23 | 4·01 | 3·30 |
| 6 O | 48 | 38·71 | 38·75 | 40·05 |
| $C^{12}H^4O^6$ | 124 | 100·00 | 100·00 | 100·00 |

So according to Laurent's view (*Compt. rend.* 26, 35); according to Piria, it is $C^{10}H^4O^5$; according to Woskressensky, $C^{25}H^9O^{13}$.

*Decomposition.* The acid burns without flame and without residue. (Piria.)

*Combinations.* Insoluble in water. (Piria.)

The acid dissolves with effervescence in alkaline carbonates, and is precipitated therefrom in its original state by stronger acids. (Piria.)

*Silver-salt.* By digesting ammonia with excess of the acid and mixing the filtrate with silver-solution, a heavy black precipitate is obtained. (Piria.)

| | | | Piria. |
|---|---|---|---|
| 12 C | 72 | 31·17 | 27·67 |
| 3 H | 3 | 1·30 | 1·95 |
| Ag | 108 | 46·75 | 48·00 |
| 6 O | 48 | 20·78 | 22·38 |
| $C^{12}H^3AgO^6$ | 231 | 100·00 | 100·00 |

The formula assumed by Laurent does not agree very well with Piria's analysis.

The acid dissolves readily in *alcohol* and in *ether.* (Piria.)

*Conjugated Compound.*

## Kinhydrone.

$$C^{24}H^{10}O^8 = C^{12}H^4O^4, C^{12}H^6O^4.$$

WÖHLER, *Ann. Pharm.* 45, 354; 51, 152.

*Green Hydrokinone, Chinhydron, grünes Hydrochinon, Hydroquinone verte, Quinhydrone.*

*Formation and Preparation.* 1. Immediately precipitated in the crystalline form, on mixing the aqueous solutions of kinone and hydrokinone. — 2. By combining aqueous kinone with a quantity of hydrogen not sufficient for the formation of hydrokinone; *e. g.* aqueous kinone mixed with sulphuric acid at the negative pole of the galvanic circuit; kinone mixed with sulphuric acid in contact with zinc; aqueous solution of kinone with gradual addition of protochloride of tin or protosulphate of iron, or sulphurous acid, or alloxantin, the latter being converted into alloxan. — 3. By the partial dehydrogenation of aqueous hydrokinone; *e. g.* when spongy platinum or animal charcoal moistened with the solution is exposed to the air; when chlorine gas is passed through aqueous hydrokinone, or that liquid is mixed with nitric acid, chromate of potash, sesquichloride of iron, or nitrate of silver. — The mixtures prepared according to (2) or (3) with concentrated solutions, assume for a while a black-red colour and then become filled with long, green, metallic-looking prisms of kinhydrone; but if the solutions are too dilute, the kinhydrone remains dissolved and is decomposed, emitting the odour of kinone. — The largest crystals are obtained by at once adding to a saturated aqueous solution of kinone (or even to its mother-liquor), a quantity of aqueous sulphurous acid just half sufficient for the formation of hydrokinone.

*Properties.* Very long and thin green prisms, having a metallic lustre (like the wings of gold-beetles or colibri, and brighter even than purpurate of ammonia), and appearing red-brown by transmitted light when strongly magnified. Melts easily to a brown liquid, and sublimes partly undecomposed in green laminæ. Smells slightly like kinone, and has a pungent taste.

| | | | Wöhler. | Schnedermann. |
|---|---|---|---|---|
| 24 C | 144 | 66·05 | 66·32 | 66·20 |
| 10 H | 10 | 4·59 | 4·64 | 4·62 |
| 8 O | 64 | 29·36 | 29·04 | 29·18 |
| $C^{24}H^{10}O^8$ | 218 | 100·00 | 100·00 | 100·00 |

*Decompositions.* 1. When kinhydrone is heated, it sublimes partly undecomposed, partly converted into yellow kinone. — 2. When it is boiled with water, kinone distils over, and the remaining dark red-brown liquid contains, together with a large quantity of hydrokinone, a brown tar, which separates, partly on cooling, partly on subsequent addition of

water. — 3. The green solution of kinhydrone in ammonia quickly assumes a dark red-brown colour on exposure to the air, and leaves a brown amorphous mass when evaporated. — 4. Kinhydrone is converted into hydrokinone by aqueous sulphurous acid, protochloride of tin, or zinc and sulphuric acid, but not by hydriodic acid or telluretted hydrogen. — 5. From a solution of nitrate of silver, on addition of ammonia, the aqueous solution of kinhydrone quickly reduces the silver.

*Combinations.* Kinhydrone dissolves sparingly in cold *water*, but abundantly and with brown-red colour in hot water, separating again as the liquid cools.

It dissolves, with green colour, in aqueous *ammonia.*

Its aqueous solution forms with *acetate of lead*, on addition of ammonia, a bright greenish yellow precipitate, quickly changing to dirty grey.

It dissolves easily, with yellow or red colour, in *alcohol* or *ether*, crystallising again in green needles as the liquid evaporates. (Wöhler.)

*Sulpho-nucleus* $C^{12}H^5(SO^2)$.

## Sulphobenzene.

$$C^{12}H^5SO^2 = C^{12}H^5(SO^2).$$

Mitscherlich. (1834.) *Pogg.* 31, 628.
H. Gericke. *Ann. Pharm.* 98, 389.

*Sulfobenzid, Sulfifune.*

*Formation and Preparation.* Produced by treating benzene with anhydrous sulphuric acid or fuming oil of vitriol (p. 183), and separates in the crystalline form when the mixture is diluted with a large quantity of water; it is then to be washed on the filter with water, dissolved in ether, left to crystallise from the filtrate, and the crystals purified by distillation. (Mitscherlich.)

*Properties.* Crystalline; melts at 100° to a transparent, colourless liquid. Boils between 360° and 440°. Inodorous. (Mitscherlich.)

| | | | Mitscherlich. |
|---|---|---|---|
| 12 C | 72 | 66·55 | 66·42 |
| 5 H | 5 | 4·59 | 4·55 |
| S | 16 | 14·68 | 14·57 |
| 2 O | 16 | 14·18 | 14·46 |
| $C^{12}H^5SO^2$ | 109 | 100·00 | 100·00 |

Gericke doubles the formula of this compound, writing it in the form of an organic radical, $\left.\begin{matrix}C^{12}H^5SO^2\\C^{12}H^5SO^2\end{matrix}\right\}$ on account of its behaviour with fuming nitric acid (p. 166). Gerhardt writes the formula: $\left.\begin{matrix}C^{12}H^5S^2O^4\\C^{12}H^5\end{matrix}\right\}$. If this were the true formula,

the body should be resolved by potash into benzene and sulphophenate of potash, according to the equation:

$$\left.\begin{matrix} C^{12}H^5S^2O^4 \\ C^{12}H^5 \end{matrix}\right\} + KHO^2 = C^{12}H^5KS^2O^6 + C^{12}H^6;$$

but no such reaction takes place, even when the compound is heated to 180° in a sealed tube with alcoholic potash for several hours. (Gericke.)

*Decompositions.* 1. Chlorine and bromine decompose sulphobenzene when heated with it, the former producing hydrochlorate of terchlorobenzene. — 2. Sulphobenzene detonates when thrown upon nitre or chlorate of potash heated considerably above the melting point, but may be distilled from these salts without decomposition. — 3. When heated with oil of vitriol, it forms a peculiar acid, whose baryta-salt is soluble in water. (Mitscherlich.) — ¶. 4. Heated with fuming nitric acid, it forms a solution from which water throws down a yellow product, separable by hot alcohol into *nitrosulphobenzene*, $\left.\begin{matrix} C^{12}XH^4SO^2 \\ C^{12}H^5SO^2 \end{matrix}\right\}$ which dissolves, and *binitrosulphobenzene*, $\left.\begin{matrix} C^{12}XH^4SO^2 \\ C^{12}XH^4SO^2 \end{matrix}\right\}$ the greater part of which remains undissolved. The latter compound is produced in much greater quantity by acting upon sulphobenzene with a mixture of sulphuric and nitric acids. (Gericke.) [Gericke's binitrosulphobenzene might, however, be regarded as nitrosulphobenzene, $C^{12}XH^4SO^2$, and his nitrosulphobenzene as a compound of $C^{12}XH^4SO^2$ with sulphobenzene $C^{12}H^5SO^2$]. ¶.

*Combinations.* Sulphobenzene dissolves but very sparingly in *water*. It dissolves in somewhat concentrated acids, and is precipitated therefrom by water. — It is insoluble in aqueous alkalis.

It dissolves in *alcohol* and *ether* and crystallises from the solutions. (Mitscherlich.)

## Yellow Sulpho-hydrokinone.

$C^{12}H^7SO^4 = C^{12}H^5(SO^2),H^2O^2$?

WÖHLER. (1845.) *Ann. Pharm.* 51, 158; 69, 295.

An alcoholic solution of kinone is saturated with sulphuretted hydrogen, which first colours it dark brown and afterwards light yellow; and the liquid, after filtration from the slender sulphur-crystals, is evaporated in vacuo:

[Perhaps thus: $C^{12}H^4O^4 + 3HS = C^{12}H^7S^2O^4 + 2S$].

If a nearly boiling aqueous solution of kinone is used, the precipitated sulphur remains mixed with the product, and appears on the filter, after washing and drying, as a pale yellow powder, which turns green on exposure to the air, and solidifies after fusion into a brown amorphous mass. — 2. Sulphuretted hydrogen is passed into brown sulpho-hydrokinone suspended in water at 60° or dissolved in alcohol, till the substance is entirely converted, with precipitation of sulphur, into a pale yellow powder;

[Perhaps thus: $C^{12}H^6S^3O^4 + HS = C^{12}H^7SO^4 + 2S$.]

In this case, sulphur remains mixed with the product. — 3. Kinone, immersed in bihydrosulphate of ammonia, forms, with evolution of heat, a yellow mass, from whose reddish-yellow solution in water previously freed from air by boiling, hydrochloric acid precipitates the compound in yellowish white flakes. — 4. Sulphuretted hydrogen is passed through water in which kinhydrone is suspended :

[Perhaps thus: $C^{24}H^{10}O^8 + 4HS = 2C^{12}H^7SO^4 + 2S$].

Prepared by (2) : Yellowish crystalline mass, which melts with partial decomposition at 100°. In the alcoholic solution it has a disagreeably harsh and hepatic taste.

| | | | Wöhler (2). |
|---|---|---|---|
| 24 C | 144 | 56·69 | 56·53 |
| 14 H | 14 | 5·52 | 4·95 |
| 2 S | 32 | 12·59 | 12·54 |
| 8 O | 64 | 25·20 | 25·98 |
| $C^{24}H^{14}S^2O^8$ | 254 | 100·00 | 100·00 |

According to Wöhler, it is $C^{12}H^6S^2O^4$, which certainly agrees better with the hydrogen-determination.

*Decompositions.* 1. Yellow sulfhydrokinone burns with the odour of sulphurous acid. — 2. Its aqueous solution deposits on evaporation, a green sulphuretted compound, and retains hydrokinone in solution. — 3. Its aqueous solution forms, with a comparatively small quantity of chlorine or sesquichloride of iron, a light brown precipitate, to which a larger quantity of chlorine imparts a yellowish red colour. Probably a mixture of sulphur- and chlorine-compounds. — 4. When immersed in an aqueous solution of kinone, it is resolved into brown sulpho-hydrokinone, hydrokinone and kinhydrone. [Perhaps in this way :

$$2C^{12}H^7SO^4 + 2C^{12}H^4O^4 = C^{12}H^6S^2O^4 + C^{12}H^6O^4 + C^{24}H^{10}O^8.]$$

*Combinations.* Dissolves sparingly in cold, more abundantly in hot *water*, which then becomes milky on cooling.

It forms a white precipitate with *neutral acetate of lead.*

Dissolves readily in *acetic* acid, *alcohol,* and *ether* forming reddish yellow solutions, and remains in the form of an amorphous residue when the solvents evaporate. (Wöhler.)

## Brown Sulpho-hydrokinone.

$C^{12}H^6S^2O^4 = C^{12}H^4(SO^2)^2,H^2.$ ?

Wöhler. (1845.) *Ann. Pharm.* 51, 157; 69, 295.

*Formation and Preparation.* Sulphuretted hydrogen gas is passed into an excess of cold aqueous solution of kinone, and the precipitated red-brown or black-brown mixture of kinhydrone and brown sulfhydrokinone treated with a small quantity of alcohol to extract the latter the former remaining for the most part undissolved; [$C^{12}H^4O^4 + 2HS = C^{12}H^6S^2O^4$.]

By evaporation of the alcoholic solution: Shining, translucent, amorphous mass; by precipitation: Dark brown amorphous powder, inodorous and tasteless, but easily fusible.

| | | | Wöhler. |
|---|---|---|---|
| 12 C | 72 | 50·71 | 51·66 |
| 6 H | 6 | 4·23 | |
| 2 S | 32 | 22·53 | 22·74 |
| 4 O | 32 | 22·53 | |
| $C^{12}H^6S^2O^4$ | 142 | 100·00 | |

According to Wöhler, it is $C^{12}H^5S^2O^4$.

Burns, with evolution of sulphurous acid.

Dissolves very readily in *alcohol*, forming a deep yellowish red solution.

### *Bromine-nucleus* $C^{12}BrH^5$.

## Bromocarbolic Acid.

$$C^{12}BrH^5O^2 = C^{12}BrH^5,O^2.$$

CAHOURS. (1845.) *N. Ann. Chim. Phys.* 13, 102.

*Bromocarbolsäure, Acide bromophénasiqué.*

Obtained by distilling a mixture of bromosalicylic acid, fine sand and a small quantity of baryta, and redistilling the distillate over sand and baryta.

Colourless liquid.

| | | | Cahours. |
|---|---|---|---|
| 12 C | 72 | 41·61 | 43·30 |
| Br | 80 | 46·24 | 44·85 |
| 5 H | 5 | 2·90 | 3·57 |
| 2 O | 16 | 9·25 | 8·28 |
| $C^{12}BrH^5O^2$ | 173 | 100·00 | 100·00 |

As the bromosalicylic acid used in the preparation was somewhat contaminated with salicylic acid, the acid analysed contained also a certain quantity of carbolic acid; hence too much C and H. (Cahours.)

### *Bromine-nucleus* $C^{12}Br^2H^4$.

## Bibromocarbolic Acid.

$$C^{12}Br^2H^4O^2 = C^{12}Br^2H^4,O^2.$$

CAHOURS. (1845.) *N. Ann. Chim. Phys.* 13, 103.

*Bibromcarbolsäure, Acide bromophénésique.*

Prepared like bromocarbolic acid, excepting that bibromosalicylic acid is used, and distilled three times over sand and baryta.

Oil, which crystallises on cooling. (Cahours.)

*Bromine-nucleus* $C^{12}Br^3H^3$.

## Terbromobenzene. $C^{12}Br^3H^3$.

MITSCHERLICH. (1835.) *Pogg.* 35, 374.
LASSAIGNE. *Rev. scient.* 5, 360.

*Tribromfune, Brombenzid, Brombenzinise.* [*Funim.*]

*Preparation.* 1. Hydrobromate of terbromobenzene is distilled with hydrate of lime or baryta. (Mitscherlich.) — 2. The same compound is boiled with alcoholic potash; the oil which is precipitated from the solution by water, dissolved in ether; the solution evaporated; the residue cooled; and the resulting mass of needles pressed between paper, and purified by recrystallisation from ether. (Lassaigne.)

*Properties.* Oil having a powerful odour. (Mitscherlich.) Silky needles, very fusible and distilling without decomposition. (Lassaigne.)

| | | | Lassaigne. |
|---|---|---|---|
| 12 C | 72 | 22·86 | 25·92 |
| 3 Br | 240 | 76·19 | |
| 3 H | 3 | 0·95 | 1·05 |
| $C^{12}Br^3H^3$ | 315 | 100·00 | |

Not decomposed by distillation over hydrate of lime. (Mitscherlich.) Very easily soluble in *alcohol* and in *ether.* (Lassaigne.)

## Hydrobromate of Terbromobenzene.
$C^{12}Br^6H^6 = C^{12}Br^3H^3,H^3Br^3$.

MITSCHERLICH. (1835.) *Pogg.* 35, 374.
LASSAIGNE. *Rev. scient.* 5, 360.

*Hydrobrom-Tribromfune, Brombenzin, Bromure de Benzine.*

*Preparation.* A mixture of benzene and bromine exposed to sunshine forms a solid compound. (Mitscherlich.) The powder thus produced in the course of 14 days by exposure to the winter sun, is freed from foreign matters by boiling with ether. (Lassaigne.)

*Properties.* White inodorous and tasteless powder, which separates from its ethereal solution by evaporation, in microscopic oblique rhombic prisms, and after fusion, solidifies in ramifications made up of rhombs set one upon the other. (Lassaigne.)

| | | | | Lassaigne. |
|---|---|---|---|---|
| 12 C | 72 | 12·90 | | 13·0 |
| 6 Br | 480 | 86·02 | | |
| 6 H | 6 | 1·08 | | 1·1 |
| $C^{12}Br^6H^6$ | 558 | 100·00 | | |

*Decompositions.* 1. When heated, it passes over partly as such (sublimed, according to Lassaigne), partly resolved into hydrobromic acid, hydrogen, bromine and terbromobenzene. — 2. When heated with hydrate of lime, it gives off terbromobenzene. (Mitscherlich.)

*Combinations.* It does not dissolve in water. (Mitscherlich.) It dissolves sparingly in *alcohol* and in *ether.* (Lassaigne.)

## Terbromocarbolic Acid.

$$C^{12}Br^3H^3O^2 = C^{12}Br^3H^3,O^2.$$

LAURENT. (1841.) *N. Ann. Chim. Phys.* 3, 211; also *Ann. Pharm.* 43, 212; also *J. pr. Chem.* 25, 415. — *Rev. scient.* 6, 74.

*Tribromcarbolsäure, Bromophänissäure, Bromindoptensäure, Acide bromophénisique.*

*Preparation.* 1. Carbolic acid immersed in excess of bromine, becomes strongly heated, gives off hydrobromic acid, and solidifies on cooling, in a brown mass, which must be boiled with water and ammonia; the solution is subsequently filtered from a small quantity of brown matter and decomposed by hydrochloric acid; and the thick precipitate washed on a filter. (Laurent.) — 2. Terbromosalicylic acid is distilled two or three times with fine sand and a small quantity of baryta. (Cahours.) —When indigo is decomposed by bromine-water and the product subsequently distilled, bromindoptene is obtained, together with a mixture (to be separated by potash) of bromindatmite (terbromaniline: *Hofmann*) which passes over, and bromindoptenic acid (terbromocarbolic acid) which remains behind. (Erdmann.)

*Properties.* Crystallises by fusion or sublimation, or from solutions, in delicate white needles. Right rhombic prisms, having the acute lateral edges truncated; $t : u = 116°$; $u : u = 52°$ and 128°. May be distilled without decomposition. Smells like terchlorocarbolic acid. (Laurent.)

| | | | Laurent. | Cahours. |
|---|---|---|---|---|
| 12 C | 72 | 21·24 | 22·55 | 22·65 |
| 3 Br | 240 | 73·16 | 71·40 | 71·60 |
| 3 H | 3 | 0·88 | 0·94 | 1·19 |
| 2 O | 16 | 4·72 | 5·11 | 4·56 |
| $C^{12}Br^3H^3O^2$ | 331 | 100·00 | 100·00 | 100·00 |

When boiled with nitric acid, it forms at first a reddish resin, which gradually disappears, and on evaporation, crystals of picric acid are obtained.

The *Terbromocarbolates* or *Bromophenisates*, when heated to redness, generally leave a metallic bromide and give off terbromocarbolic acid [?].

The *Ammonia-salt* crystallises in needles.

Its solution forms with concentrated chloride of *barium* or chloride of *strontium*, a precipitate composed of needles; with *neutral acetate of lead*, a white precipitate; with *cupric* acetate, a red-brown precipitate soluble in alcohol; and with nitrate of *silver*, an orange-yellow precipitate.

The acid dissolves in *alcohol*, but somewhat less than terchlorocarbolic acid. (Laurent.)

*Substance isomeric with Terbromocarbolic acid.*

A concentrated aqueous solution of salicylate of potash mixed with a small quantity of potash and then with a large quantity of bromine, becomes heated and decolorised, gives off carbonic acid, and soon deposits a kermes-brown substance, which is insoluble in water, ammonia, cold potash, and alcohol, but dissolves with extreme facility in ether; it contains, after washing and drying, 22·19 p. c. C, 71·8 Br and 0·88 H; and, when heated, gives off white vapours, which condense into delicate white needles of terbromocarbolic acid. (Cahours, *N. Ann. Chim. Phys.* 13, 43.)

¶. *Oxybromine-nucleus* $C^{12}Br^2H^2O^2$.

## Bromanilic Acid.

$$C^{12}Br^2H^2O^8 = C^{12}Br^2H^2O^2,O^6.$$

STENHOUSE. *Phil. Mag. J.* [4], 8, 39.

When bromanil is thrown into hot potash-ley, it immediately dissolves, forming a deep purple solution which quickly deposits brownish red needles of bromanilate of potash; and on adding sulphuric or hydrochloric acid to an aqueous solution of this salt, or to a solution of bromanil in hot potash-ley, the purple colour immediately disappears, and bromanilic acid is gradually deposited, in beautiful, shining, reddish crystalline scales, becoming bronze-coloured when dry. — The acid appears also to be formed by slow digestion of bromanil in water.

| *Acid.* | | | Stenhouse. |
|---|---|---|---|
| 12 C | 72 | 24·16 | |
| 2 Br | 160 | 53·69 | 53·91 |
| 2 H | 2 | 0·69 | |
| 8 O | 64 | 21·46 | |
| $C^{12}Br^2H^2O^8$ | 298 | 100·00 | |

| *Potash-salt.* | | | Stenhouse. |
|---|---|---|---|
| 12 C | 72·0 | 18·35 | |
| 2 Br | 160·0 | 40·77 | 40·87 |
| 2 H | 2·0 | 0·51 | |
| 2 K | 78·4 | 19·98 | 19·78 |
| 10 O | 80·0 | 20·39 | |
| $C^{12}Br^2K^2O^8 + 2Aq$ | 392·4 | 100·00 | |

The potash-salt dissolves readily in water, but is nearly insoluble in alcohol.

*Oxy-bromine-nucleus* $C^{12}Br^4O^2$.

## Bromanil.

$C^{12}Br^4O^4 = C^{12}Br^4O^2,O^2$.

STENHOUSE. *Phil. Mag. J.* [4], 8, 38.

*Formation and Preparation.* Picric acid is digested with water and bromine for several hours in an apparatus in which the condensed vapours can flow back again, the bromine being also replaced as it evaporates. Bromanil is then produced together with bronopicrin and hydrobromic acid :

$$\underbrace{2C^{12}X^3H^3O^2}_{\text{picric acid.}} + 28Br = \underbrace{C^{12}Br^4O^4}_{\text{bromanil.}} + \underbrace{6C^2XBr^3}_{\text{bromopicrin.}} + 6HBr.$$

The small quantity of gas evolved, increasing somewhat towards the end of the operation, contains no carbonic acid, but consists chiefly of nitrogen and its oxides, particularly nitric oxide, probably formed by decomposition of the bromopicrin. — On distilling the product, bromopicrin passes over, and bromanil remains together with undecomposed picric acid. On dissolving out the latter with hot water, the bromanil remains in yellowish red crystalline scales contaminated with a small quantity of a reddish resinous substance, from which the bromanil may be freed by recrystallisation from alcohol.

*Properties.* Golden-yellow crystalline scales, which melt into a brownish liquid when heated, and sublime in sulphur-yellow crystals.

| | | | Stenhouse. |
|---|---|---|---|
| 12 C | 72 | 16·98 | 17·16 |
| 4 Br | 320 | 75·47 | 75·73 |
| 4 O | 32 | 7·55 | 7·11 |
| $C^{12}Br^4O^4$ | 424 | 100·00 | 100·00 |

Bromanil is converted by sulphurous acid into bromhydranil.

It is nearly insoluble in *water*, slightly soluble in cold, but tolerably soluble in hot *alcohol* and *ether*. (Stenhouse.)

## Bromhydranil.

$C^{12}Br^4H^2O^4 = C^{12}Br^4O^2,H^2O^2$.

STENHOUSE. *Phil. Mag. J.* [4], 8, 39.

When sulphurous acid gas is passed through hot alcohol containing an excess of bromanil, the latter gradually dissolves, forming a colourless

solution, which when sufficiently concentrated, deposits bromhydranil in colourless crystals having a mother-of-pearl lustre. The compound is also formed by boiling bromanil in aqueous sulphurous acid, but very slowly, because both bromanil and bromhydranil are nearly insoluble in water.

Bromhydranil, when heated, melts and readily sublimes, forming soft colourless scales.

| | | | Stenhouse. |
|---|---|---|---|
| 12 C | 72 | 16·90 | 17·14 |
| 4 Br | 320 | 75·12 | |
| 2 H | 2 | 0·47 | 0·55 |
| 4 O | 32 | 7·51 | |
| $C^{12}Br^4H^2O^4$ | 426 | 100·00 | |

Bromhydranil is nearly insoluble in *water*, but dissolves abundantly in *alcohol* and *ether*. From its concentrated alcoholic solution, it is precipitated by water in the form of a white crystalline powder. (Stenhouse.) ¶.

### *Chlorine-nucleus* $C^{12}ClH^5$.

## Chlorobenzene or Chloride of Phenyl.

$$C^{12}ClH^5 = C^{12}H^5,Cl.$$

LAURENT & GERHARDT. (1849.) *Compt. Chim.* 1849, 429: abstr. *Ann. Pharm.* 75, 79.
WILLIAMSON & SCRUGHAM. *Chem. Soc. Qu. J.* 7, 238; *Proc. Roy. Soc.* 7, 18.

*Chlorfune, Chlorphenyl.*

*Formation and Preparation.* By decomposing carbolic acid with pentachloride of phosphorus, washing the resulting heavy oil with water and potash, and rectifying. (Laurent & Gerhardt.) — ¶. When 2 At. pentachloride of phosphorus are added by small portions to 5 At. carbolic acid, a violent action takes place at first, great heat being developed and hydrochloric acid evolved: but this action soon ceases and it becomes necessary to heat the mixture. If it be then distilled upwards till it has nearly ceased to give off hydrochloric acid, and the distillate subsequently collected, about $\frac{2}{3}$ of the whole distils over below 240°, and the temperature then rapidly rises above the range of the mercurial thermometer. The distillate collected below 240° is a limpid colourless liquid, which when washed with hot water and subsequently with potash, yields a thick oil which settles to the bottom of the vessel; and on submitting this oil to fractional distillation, collecting apart the portion which passes over at 136° to 138°, chloride of phenyl is obtained, nearly pure but in small quantity. The brown liquid which distils above the range of the thermometer is phosphate of phenyl, and constitutes by far the largest portion of the product. When an excess of chloride of phosphorus is

used in the preparation, the quantity of chloride of phenyl obtained appears to be still smaller than with the above proportions. (Williamson & Scrugham.) ¶.

*Properties.* Heavy oil, which, after washing with water and potash, and subsequent rectification, is destitute of odour. (Laurent & Gerhardt.) Colourless, mobile liquid, having a fragrant odour. Boils at 136°. (W. & S.)

| | | | Laurent & Gerhardt. | Scrugham. |
|---|---|---|---|---|
| 12 C | 72·0 | 64·06 | 67·2 | 66·58 |
| Cl | 35·4 | 31·49 | | 30·83 |
| 5 H | 5·0 | 4·45 | 5·2 | 4·93 |
| $C^{12}ClH^5$ | 112·4 | 100·00 | | 102·34 |

[The product examined by Laurent & Gerhardt was probably impure.]

*Decompositions.* Distils at a somewhat high temperature, for the most part undecomposed. By water, and more quickly by aqueous potash it is converted into carbolic acid: $C^{12}ClH^5 + KO + HO = C^{12}H^6O^2 + KCl$. (Laurent & Gerhardt.)

### ¶. *Conjugated Compounds of Chlorobenzene.*

## Sulphite of Chlorobenzene.

$C^{12}ClH^5S^2O^4 = C^{12}ClH^5,2SO^2$. ?

GERHARDT & CHANCEL. *Compt. rend.* 35, 690.

*Chlorure phényl-sulfureux, Chlorure de sulfophényle.*

Obtained by distilling a sulphobenzolate with oxychloride of phosphorus. Benzene is gently heated with an equal volume of oil of vitriol till it is completely dissolved, and a homogeneous red liquid obtained. Water is then added; the liquid saturated with chalk; the filtered solution of sulphobenzolate of lime mixed with a quantity of carbonate of soda just sufficient to precipitate all the lime; and the resulting solution of sulphobenzolate of soda filtered and evaporated to dryness. The soda-salt, after having been heated for some time in a stove to about 150°, is introduced into a tubulated retort, and mixed with oxychloride of phosphorus to the consistence of a thick paste, the materials being introduced in alternate small portions, because the action begins even at ordinary temperatures and is attended with considerable evolution of heat. The mixture is then distilled as long as any oily liquid passes over, and the product rectified, the last portions which distil over at 254°, after the thermometer has become stationary, being collected apart as the pure product. The portion which distils over below 254° contains a considerable quantity of sulphite of chlorobenzene carried over with the vapours of oxychloride of phosphorus, and may be used for the preparation of sulphite of amidobenzene. Sulphobenzolate of soda is better adapted than the lime-salt for the preparation of sulphite of chlorobenzene, because it is more readily acted upon by the oxychloride of phosphorus.

Colourless, strongly refracting oil, of sp. gr. 1·378 at 23°. Fumes slightly in the air. Has a rather powerful odour resembling that of bitter almonds. Boils constantly at 254°.

| *Calculation.* | | |
|---|---|---|
| 12 C | 72·0 | 40·82 |
| 5 H | 5·0 | 2·83 |
| Cl | 35·4 | 20·07 |
| 2 S | 32·0 | 18·14 |
| 4 O | 32·0 | 18·14 |
| $C^{12}ClH^5S^2O^4$ | 176·4 | 100·00 |

Might also be regarded as $C^{12}ClH^3(SO^2)^2,H^2$ or as chloride of sulphobenzene $C^{12}H^5S^2O^4,Cl$.

This compound is but little acted upon by water, which however renders it acid. The fixed alkalis decompose it immediately, forming an alkaline chloride and a sulphobenzolate:

$$[C^{12}ClH^5,2SO^2 + 2KO = KCl + C^{12}H^5K,2SO^3.]$$

Ammonia converts it into sulphite of amidobenzene, (or sulphophenylamide) and chloride of ammonium:

$$[C^{12}ClH^5,2SO^2 + 2NH^3 = C^{12}AdH^5,2SO^2 + NH^4Cl.]$$

Sulphite of chlorobenzene is insoluble in water, but dissolves very readily in *alcohol*. (Gerhardt & Chancel.)

## Chlorosulphobenzolic Acid.

$$C^{12}ClH^5S^2O^6 = C^{12}ClH^5,2SO^3.$$

L. Hutchings. *Chem. Soc. Qu. J.* x. 101.

*Sulphate of Chlorobenzene, Sulphate of Phenylic Chloride.*

Obtained by the action of fuming sulphuric acid on chlorobenzene. The liquids gradually combine at ordinary temperatures; and on treating the mixture with excess of milk of lime, a soluble lime-salt is obtained which crystallises in microscopic tabular crystals.

| *Lime-salt.* | | | Hutchings. |
|---|---|---|---|
| 12 C | 72·0 | 34·03 | |
| 4 H | 4·0 | 1·92 | |
| Ca | 20·0 | 9·46 | 9·26 |
| Cl | 35·4 | 16·78 | |
| 2 S | 32·0 | 15·13 | 15·22 |
| 6 O | 48·0 | 22·68 | |
| $C^{12}ClH^4Ca,2SO^6$ | 211·4 | 100·00 | ¶. |

## Chloroniceic Acid.

$$C^{12}ClH^5O^4 = C^{12}ClH^5,O^4.$$

St. Evre. (1849.) *N. Ann. Chim. Phys.* 25. 484; also *Ann. Pharm.* 70, 257; also, *J. pr. Chem.* 46, 449; *Compt. rend.* 25, 912.

*Chlornicensäure, Chlorniceinsäure, Acide nicéique monochloré, Acide chloronicéique.*

*Formation and Preparation.* Chlorine gas is passed for about two days in the cold through a solution of 1 pt. benzoic acid and 33 pts. hydrate of potash, by means of a tube widened at the end and thereby prevented from getting stopped up, till the liquid, which continually gives off carbonic acid gas, first turns yellow, greenish yellow and light green, then again yellow, and deposits a thick green crystalline magma of chloroniceate, chlorate, and a small quantity of benzoate of potash, above which there floats a solution of benzoate of potash and chloride of potassium. The entire mass is gently heated with an equal quantity of water; saturated with carbonic acid; mixed with a small quantity of hydrochloric acid; heated to the boiling point, whereby the whole of the saline matter is dissolved, and the chloroniceic acid separated in the form of a yellowish oil, which rises to the surface or sinks to the bottom and soon crystallises; the watery liquid separated therefrom; and the chloroniceic acid freed from admixed benzoic acid, partly by fusion under water, partly by repeated crystallisation from alcohol or a mixture of ether and alcohol. From the benzoic acid obtained in this part of the process, as well as from the aqueous solution, an additional portion of chloroniceic acid may be prepared by fusion under water.

*Properties.* Microscopic four-sided needles united in cauliflower-like masses; melts at 100°, and in this state has a density of 1·29; boils at 215°, volatilising undecomposed, and subliming in flat needles, having a fatty lustre and united in stellate groups. In the melted state, it has a penetrating odour.

| | | | St. Evre. |
|---|---|---|---|
| 12 C | 72·0 | 49·86 | 50·35 |
| Cl | 35·4 | 24·51 | 23·81 |
| 5 H | 5·0 | 3·47 | 3·36 |
| 4 O | 32·0 | 22·16 | 22·48 |
| $C^{12}ClH^5O^4$ | 144·4 | 100·00 | 100·00 |

*Decompositions.* 1. Fuming nitric acid quickly dissolves chloroniceic acid, with violent action, and deposits crystals of nitrochloroniceic acid, $C^{12}ClXH^4O^4$, while the mother-liquor retains the acid $C^{10}ClXH^4,O^4$. — 2. The mixture of the acid with fuming oil of vitriol forms a soluble baryta-salt, and therefore probably contains $C^{12}ClH^5O^4,2SO^3$. — 3. When the acid is distilled with excess of baryta or lime, a residue is left consisting of metallic chloride, alkaline carbonate and charcoal, while chloronicene, $C^{10}ClH^5$, passes over in the form of a brownish yellow distillate, and then paranicene $C^{20}H^{12}$, as a lemon-yellow sublimate. The acid is not acted upon by chlorine gas, even with the aid of heat, or by potassium-amalgam.

*Combinations.* The acid does not dissolve in water.

*Chloroniceate of Ammonia.* — The acid dissolved in alcohol and saturated with ammonia, yields broad micaceous laminæ, which are fusible and volatilise without decomposition. When exposed to light, they assume a brown colour and turn acid.

| | | | St. Evre. |
|---|---|---|---|
| 12 C | 72·0 | 44·61 | 45·00 |
| N | 14·0 | 8·67 | 8·90 |
| Cl | 35·4 | 21·93 | |
| 8 H | 8·0 | 4·96 | 5·29 |
| 4 O | 32·0 | 19·83 | |
| $C^{12}ClH^4(NH^4)O^4$ | 161·4 | 100·00 | |

*Chloroniceate of Baryta.* — White crystalline powder, which at a red heat, gives off the two hydrocarbons above mentioned, leaving a carbonaceous residue; dissolves sparingly in water and pretty easily in hot alcohol.

| | | | St. Evre. |
|---|---|---|---|
| 12 C | 72·0 | 33·96 | 33·78 |
| Cl | 35·4 | 16·70 | |
| 4 H | 4·0 | 1·89 | 2·21 |
| Ba | 68·6 | 32·36 | 32·83 |
| 4 O | 32·0 | 15·09 | |
| $C^{12}ClH^4BaO^4$ | 212·0 | 100·00 | |

*Chloroniceate of Silver.* — The alcoholic ammonia-salt added to an alcoholic solution of nitrate of silver, throws down white flakes which, after washing, dry up to a soft crystalline powder.

| | | | St. Evre. |
|---|---|---|---|
| 12 C | 72·0 | 28·64 | 29·21 |
| Cl | 35·4 | 14·08 | |
| 4 H | 4·0 | 1·59 | 2·05 |
| Ag | 108·0 | 42·96 | 43·21 |
| 4 O | 32·0 | 12·73 | |
| $C^{12}ClH^4AgO^4$ | 251·4 | 100·00 | |

The acid dissolves in alcohol. (St. Evre.)

## Chloroniceamide.

$$C^{12}NClH^6O^2 = C^{12}ClAdH^4,O^2.$$

*Amide chloronicéique, Chloronicenamid.*

Obtained by placing an alcoholic solution of chloroniceic ether and ammonia together in a bottle for some time, and then evaporating to the crystallising point.

Colourless laminæ having a fatty lustre and melting at 108°. (St. Evre, *N. Ann. Chim. Phys.* 25, 492.)

| | | | St. Evre. |
|---|---|---|---|
| 12 C | 72·0 | 50·21 | 50·51 |
| N | 14·0 | 9·76 | 9·58 |
| Cl | 35·4 | 24·69 | |
| 6 H | 6·0 | 4·18 | 4·27 |
| 2 O | 16·0 | 11·16 | |
| $C^{12}NClH^{6}O^{2}$ | 143·4 | 100·00 | |

*Conjugated Compound.*

## Chloroniceic Ether.

$$C^{16}ClH^{9}O^{4} = C^{4}H^{5}O,C^{12}ClH^{4}O^{3}.$$

Obtained by passing hydrochloric acid gas through an alcoholic solution of chloroniceic acid, and rectifying the ether over litharge.

Colourless liquid, of sp. gr. 0·981, boiling at 230°.

Its alcoholic solution is gradually converted by ammonia into chloroniceamide:

$$C^{16}ClH^{9}O^{4} + NH^{3} = C^{12}NClH^{6}O^{2} + C^{4}H^{6}O^{2}.$$

(St. Evre, *N. Ann. Chim. Phys.* 25, 491.)

| | | | St. Evre. |
|---|---|---|---|
| 16 C | 96·0 | 55·68 | 55·99 |
| Cl | 35·4 | 20·54 | 20·23 |
| 9 H | 9·0 | 5·22 | 5·20 |
| 4 O | 32·0 | 18·56 | 18·58 |
| $C^{16}ClH^{9}O^{4}$ | 172·4 | 100·00 | 100·00 |

*Chlorine-nucleus* $C^{12}Cl^{2}H^{4}$.

## Bichlorocarbolic Acid.

$$C^{12}Cl^{2}H^{4}O^{2} = C^{12}Cl^{2}H^{4},O^{2}.$$

LAURENT. (1836.) *Ann. Chim Phys.* 63, 27; also *Ann. Pharm.* 23, 60; also *J. pr. Chem.* 10, 293.—*Ann. Chim. Phys.* 3, 210; also *Ann. Pharm.* 43, 212; also *J. pr. Chem.* 25, 414.

*Bichlorcarbolsäure, Chlorphänessäure, Acidê chlorophênêsique.*

*Formation.* 1. By the comparatively feeble action of chlorine on carbolic acid. (Laurent.)—2. By distilling bichlorosalicylic acid three times with fine sand and a small quantity of baryta or lime. (Cahours.)

*Preparation.* Coal-tar is distilled till the distillate begins to exhibit a viscid consistence; chlorine gas passed through the yellowish oil for a day; the liquid then cooled to − 10°, and strained through linen to separate the naphthalin which has crystallised out; chlorine again passed for two days through the liquid, which is then cooled to 0°, decanted

from the crystallised hydrochlorate of bichloronaphthalin ($C^{20}Cl^2H^6,H^2Cl^2$) and distilled (whereupon it froths up considerably, giving off a large quantity of chlorine and afterwards hydrochloric acid) till the thick black residue exhibits considerable intumescence (quadrochloronaphthalin then subliming in needles); the distillate shaken up in a bottle with oil of vitriol as long as hydrochloric acid continues to escape; the rose-coloured oil of vitriol (which deposits a stinking substance when neutralized) removed by the syphon; the remaining oil washed with a large quantity of water, and mixed in the flask with ammonia, with which it solidifies completely into a white mass, with slight rise of temperature; this mass boiled with water; the solution decanted hot from a brown oil, which is again to be treated with ammonia and then with hot water to remove the acids completely; the hot-filtered aqueous solutions, containing bi- and ter-chlorocarbolate of ammonia, mixed by drops with dilute nitric acid till a slight turbidity is produced; the liquid filtered from the red-brown precipitate; the filtrate precipitated with a slight excess of nitric acid; the white precipitate, which is gelatinous at first but afterwards curdy and consists of fine needles, collected on a filter, and distilled after washing, pressing and drying; and the distillate boiled with a slight excess of aqueous carbonate of soda, which leaves behind the oily bichlorocarbolic acid, whilst the crystalline terchlorocarbolic acid is precipitated from the filtrate by nitric acid, and purified by distillation. (Laurent.)

*Properties.* 1. Oil, which volatilises without residue, and has a peculiar odour. (Laurent.)

| | | | Laurent. |
|---|---|---|---|
| 12 C | 72·0 | 44·23 | 41·49 |
| 2 Cl | 70·8 | 43·49 | 43·00 |
| 4 H | 4·0 | 2·46 | 2·82 |
| 2 O | 16·0 | 9·82 | 12·69 |
| $C^{12}Cl^2H^4O^2$ | 162·8 | 100·00 | 100·00 |

*Decompositions.* 1. By the further action of chlorine, the acid is converted, with evolution of hydrochloric acid, into terchlorocarbolic acid.

$$C^{12}Cl^2H^4O^2 + 2Cl = C^{12}Cl^3H^3O^2 + HCl.$$

2. When boiled with nitric acid, it forms very volatile needles. (Laurent.)

*Combinations.* Insoluble in water.

When aqueous ammonia is poured upon the acid, it immediately solidifies into a crystalline mass, which however on exposure to the air, gives off ammonia and becomes oily, but solidifies when again treated with ammonia. The solid salt is soluble in water.

The acid dissolves with great facility in *alcohol* and in *ether*. (Laurent.)

*Chlorine-nucleus* $C^{12}Cl^3H^3$.

## Terchlorobenzene.

$C^{12}Cl^3H^3$.

MITSCHERLICH. *Pogg.* 35, 372.
LAURENT. *Ann. Chim. Phys.* 63, 27; also *Ann. Pharm.* 23, 69.

*Trichlorfune, Chlorobenzid, Chlorophénise.* — Observed by Faraday in 1825; more distinctly recognized by Mitscherlich in 1833.

*Preparation.* 1. By distilling a mixture of hydrochlorate of terchlorobenzene and excess of hydrate of lime or baryta. — 2. By distilling hydrochlorate of terchlorobenzene by itself in a tall flask, in which the portion that rises undecomposed can constantly run back again. (Mitscherlich.) — 3. By boiling hydrochlorate of terchlorobenzene for some minutes with alcoholic potash, mixing with water, boiling the oil thereby precipitated with fresh alcoholic potash, precipitating again with water, drying over chloride of calcium, and rectifying. (Laurent.)

*Properties..* Colourless oil of sp. gr. 1·457 at 7°. Boils at 210° Vapour-density 6·37. (Mitscherlich.)

| | | | Mitscherlich. | Laurent. |
|---|---|---|---|---|
| 12 C | 72·0 | 39·73 | 39·91 | 38·89 |
| 3 Cl | 106·2 | 58·62 | | |
| 3 H | 3·0 | 1·65 | 1·62 | 1·72 |
| $C^{12}Cl^3H^3$ | 181·2 | 100·00 | | |

| | Vol. | Density. |
|---|---|---|
| C-vapour | 12 | 4·9920 |
| Cl-gas | 3 | 7·3629 |
| H-gas | 3 | 0·2079 |
| Vapour of $C^{12}Cl^3H^3$ | 2 | 12·5628 |
| | 1 | 6·2814 |

Its vapour decomposes at a red heat. — Chlorine, bromine, acids and alkalis (even hydrate of lime and baryta when it is distilled with them) exert no decomposing action upon it.

It is insoluble in water, but dissolves very easily in *alcohol, ether,* and *benzene.*

## Hydrochlorate of Terchlorobenzene.

$C^{12}Cl^6H^6 = C^{12}Cl^3H^3,H^3Cl^3$.

MITSCHERLICH. (1835.) *Pogg.* 35, 370.
PELIGOT. *Ann. Chim. Phys.* 56, 66.
LAURENT. *Ann. Chim. Phys.* 63, 27; also *Ann. Pharm.* 23, 68.

*Hydrochlor - Trichlorfune, Chlorbenzin, Chlorobenzone, Hydrochlorate de Chlorophénise.*

*Formation.* (p. 138).

*Preparation.* When chlorine-gas is passed in sunshine into a capacious bottle containing a small quantity of benzene, the chlorine is absorbed, with rise of temperature and formation of white vapours; and crystals of hydrochlorate of terchlorobenzene shoot out from the benzene, which in the end is completely converted into the hydrochlorate. Nevertheless, a certain quantity of terchlorobenzene remains mixed with it, because the heat causes part of the hydrochloric acid to separate; on this account, the crystals must be washed with a little ether (Mitscherlich), or purified by crystallisation from hot alcohol. (Peligot.)

*Properties.* Transparent, colourless, shining laminæ. (Peligot.) Right rhombic prisms with the acute lateral edges truncated. (Laurent.) Melts at 132°, and, if then gradually cooled, begins to solidify at 125°, its temperature then rising again to 132°. (Mitscherlich.) Melts at 135° to 140° (Laurent); melts into an oil which begins to solidify at 50°. (Peligot.) Distils completely at 288°, but is at the same time partially decomposed into hydrochloric acid and terchlorobenzene. (Mitscherlich.) Boils at 150°, and the distillate smells of chlorine and bitter almonds. (Peligot.)

| | | | Mitscherlich. | Peligot. | Laurent. |
|---|---|---|---|---|---|
| 12 C | 72·0 | 24·79 | 24·95 | 25·55 | 24·97 |
| 6 Cl | 212·4 | 73·14 | | | |
| 6 H | 6·0 | 2·07 | 2·02 | 2·33 | 2·28 |
| $C^{12}Cl^6H^6$ | 290·4 | 100·00 | | | |

It is resolved, partially when heated by itself, and completely when heated with hydrate of lime, into terchlorobenzene and hydrochloric acid r chloride of calcium.

It is insoluble in water. (Mitscherlich; Peligot.)

Dissolves sparingly in cold alcohol (Mitscherlisch); readily in hot lcohol. (Peligot.)

Dissolves more abundantly in ether, and yields definite crystals when the ether evaporates. (Mitscherlich.)

## Terchlorocarbolic Acid.

$C^{12}Cl^3H^3O^2 = C^{12}Cl^3H^3,O^2$.

Laurent. (1836.) *Ann. Chim. Phys.* 63, 27; also *Ann. Pharm.* 23, 60; also *J. pr. Chem.* 10, 293. — *N. Ann. Chim. Phys.* 3, 206; also *Ann. Pharm.* 43, 208; also *J. pr. Chem.* 25, 410. — *N. Ann. Chim. Phys.* 3, 497.

Erdmann. *J. pr. Chem.* 19, 332; 22, 276; 25, 472.

Piria. *N. Ann. Chim. Phys.* 142, 269.

*Trichlorcarbolsäure, Chlorphänissäure, Chlorindoptensäure, Acide chlorophénisique.*

*Formation.* 1. By the action of chlorine on carbolic or bichlorocarbolic acid (Laurent); or by the short action of chlorate of potash and hydrochloric acid on carbolic acid. (Hofmann.) — 2. In the decomposition of aniline by chlorine. (Hofmann.) — 3. Also of an aqueous solution of saligenin. (Piria.) — 4. In the decomposition of indigo suspended in water by chlorine.

*Preparation.* 1. Either by the method given on pages 178, 179; or better: By repeatedly distilling the commercial oil obtained from coal-tar; collecting apart the portion which boils between 170 and 190°; separating it out from the naphthaline which crystallises out in the cold; passing chlorine-gas through it for a day or two according to the quantity; distilling it till nothing but a carbonaceous residue is left (whereby hydrochloric acid is given off and a very offensive odour emitted), the receiver being changed at certain stages of the process, and the first and last portions of the distillate set aside; passing chlorine through the middle distillate till it solidifies into a crystalline paste; purifying this mass from adhering oil by spreading it on paper and pressing it; dissolving the crystalline mass—which, besides the terchlorocarbolic acid, likewise contains a little oil and crystalline chloralbin ($C^{12}Cl^2H^8$)—in boiling water containing ammonia; filtering; dissolving in water the terchlorocarbolate of ammonia which has crystallised out on cooling; mixing the solution with hydrochloric acid to precipitate the terchlorocarbolic acid; and purifying this product by washing, drying, and distillation. — (Laurent.)

2. When chlorine gas is passed through an aqueous solution of saligenin, the bottle being frequently closed and shaken, the liquid immediately becomes turbid, then deposits a yellow, afterwards reddish and finally orange-yellow crystalline resin, and a white, bulky, crystalline precipitate. To free the entire precipitate from a closely adhering reddish oil, it is distilled three or four times with oil of vitriol, which carbonises the oil, with evolution of sulphurous and hydrochloric acid, and ultimately pure terchlorocarbolic acid distils over. (Piria.)

3. By passing chlorine-gas through water in which indigo is suspended, and distilling the yellowish red magma, with cohobation of the watery distillate, a small quantity of chlorindoptene is obtained sublimed in laminæ and needles. Now, when this mixture of terchlorocarbolic acid and chlorindatmite (terchloraniline: *Hofmann*) is distilled with potash, the chlorindatmite passes over, while crystallised chlorindoptate of potash remains behind, mixed with free potash. This residue is pressed, exposed to the carbonic acid in the air, dissolved in the smallest possible quantity of boiling alcohol, and left to crystallise after filtration; and from the aqueous solution of the capillary crystals thus obtained, the chlorindoptenic acid is precipitated by acids. (Erdmann.)

*Properties.* Crystallises from solutions—best from rock-oil—or by sublimation, in white needles and prisms having a silky lustre. Right rhombic prisms with the acute lateral edges truncated; $u : u = 70°$ and $110°$; $u : t = 145°$. Melts at 44° to a colourless oil (at 58° to a transparent oil of the colour of olive-oil: *Piria*; to a colourless oil: *Hofmann*), and on cooling solidifies in a radiated mass (translucent: *Piria*; exactly like stearic acid: *Hofmann*). Boils at 250° (at 156°: *Piria*), and volatilises undecomposed; when kept for a year, it sublimes in needles even at

ordinary temperatures. Has a penetrating, and very persistent disagreeable odour. (Laurent.) Reddens litmus strongly. (Erdmann.)

| | | | Laurent. | | Erdmann. | | Piria. |
|---|---|---|---|---|---|---|---|
| | | *Distilled.* | *Earlier.* | *Later.* | *Earlier.* | *Later.* | |
| 12 C | 72·0 | 36·51 | 36·10 | 36·98 | 38·02 | 36·61 | 35·91 |
| 3 Cl | 106·2 | 53·85 | 50·00 | 52·80 | 54·53 | | 53·46 |
| 3 H | 3·0 | 1·53 | 1·89 | 1·61 | 1·77 | 1·68 | 1·84 |
| 2 O | 16·0 | 8·11 | 12·01 | 8·61 | 5·68 | | 8·79 |
| $C^{12}Cl^3H^3O^2$ | 197·2 | 100·00 | 100·00 | 100·00 | 100·00 | | 100·00 |

*Decompositions.* 1. The acid is easily set on fire and burns with a green-edged smoky flame, emitting hydrochloric acid vapours. (Laurent.) — 2. Chlorine converts it into quintichlorocarbolic acid, but slowly and only when aided by heat. (Laurent.) — 3. With strong nitric acid, it assumes a brown-red colour, froths up violently, and after continued boiling, yields, on cooling, golden-yellow inodorous scales which easily melt and sublime. (Laurent.) — 4. Heated with chlorate of potash and hydrochloric acid, it is converted into chloranil. (Hofmann.)

$$C^{12}Cl^3H^3O^2 + 4Cl + 2O = C^{12}Cl^4O^4 + 3HCl.$$

*Combinations.* The acid is insoluble in *water* (Laurent); nearly insoluble in cold, sparingly insoluble in boiling water. (Piria.)

It dissolves readily in warm fuming *oil of vitriol* and solidifies with it on cooling into a mass consisting of needles. (Laurent.)

The *Terchlorocarbolates* or *Chlcrophenisates* give off terchlorocarbolic acid by dry distillation, leaving a metallic chloride and charcoal. They burn with a smoky, green-edged flame. Nitric acid added to these solutions, throws down the terchlorocarbolic acid in the form of a bulky mass. (Laurent.)

*Terchlorocarbolate of Ammonia.* — The solution of the acid in aqueous ammonia, yields needles which have a slight alkaline reaction, and sublime completely when exposed to the heat of the sun, but by dry distillation in a retort, are partially resolved into nitrogen, ammonia, terchlorocarbolic acid, bichlorocarbolic acid, and sal-ammoniac. The salt dissolves very sparingly in cold, very easily in hot water, or in water containing alcohol. (Laurent.)

| | *Needles, dried in vacuo.* | | Laurent. |
|---|---|---|---|
| 12 C | 72·0 | 33·62 | 34·01 |
| N | 14·0 | 6·53 | 7·20 |
| 3 Cl | 106·2 | 49·58 | 49·83 |
| 6 H | 6·0 | 2·80 | 2·50 |
| 2 O | 16·0 | 7·47 | 6·16 |
| $C^{12}Cl^3H^2(NH^4)O^2$ | 214·2 | 100·00 | 100·00 |

*Terchlorocarbolate of Potash.* — Very soluble needles. (Erdmann.)

*Terchlorocarbolate of Soda.* — Very soluble needles having a silky lustre. (Laurent.)

*Terchlorocarbolate of Baryta.*—The ammonia-salt precipitates chloride of barium only from somewhat concentrated solutions;—from cold solutions the salt separates as a jelly; but from hot solutions, in long silky

needles. These crystals, after drying in vacuo at 100°, contain 28·82 p.c. baryta, and are therefore $C^{12}Cl^3H^2BaO^2$. When subjected to dry distillation, they give off the greater part of the acid undecomposed, but leave a residue of chloride of barium. They dissolve sparingly in water.

The ammonia-salt throws down from concentrated (not from dilute) solutions of *chloride of calcium*, and likewise of *alum*, a white jelly; it precipitates *neutral acetate of lead* and *ferrous salts*, white; ferric salts, reddish (*cobaltous salts*, reddish; *nickel-salts*, greenish, according to Erdmann); *cupric salts*, brown-red (dark-purple violet, according to Erdmann and Hofmann), the precipitate dissolving with brown colour in hot alcohol, and crystallising on cooling, in brown, shining, oblique rectangular prisms (*mercurous* nitrate, white, according to Erdmann); *mercuric chloride*, yellowish white; curdy; and nitrate of *silver*, lemon-yellow. (Laurent.)

| | | | Erdmann. at 120°. | Laurent. at 100°. |
|---|---|---|---|---|
| | *Silver precipitate.* | | | |
| 12 C | 72·0 | 23·67 | 24·93 | |
| 3 Cl | 106·2 | 34·91 | 35·32 | |
| 2 H | 2·0 | 0·66 | 0·95 | |
| Ag | 108·0 | 35·50 | 36·36 | 35·18 |
| 2 O | 16·0 | 5·26 | 2·44 | |
| $C^{12}Cl^3H^2AgO^2$ | 304·2 | 100·00 | 100·00 | |

The acid dissolves in *wood-spirit*, and with extreme facility in *alcohol* and in *ether;* the alcoholic solution, on addition of water, deposits oily drops which gradually solidify; from the solution in hot, extremely dilute alcohol, the acid crystallises on cooling. (Laurent.)

It dissolves very readily in *oils*, both *fixed* and *volatile*. (Piria.)

## *Chlorine-nucleus* $C^{12}Cl^5H$.

# Quintichlorocarbolic Acid.

$$C^{12}Cl^5HO^2 = C^{12}Cl^5H,O^2.$$

ERDMANN. (1841.) *J. pr. Chem.* 22, 272.
LAURENT. *N. Ann. Chim. Phys.* 3, 497.

*Quintichlorcarbolsäure, Chlorphänussäure, gechlorte Chlorindoptensäure, Acid chlorophénusique.*

*Formation.* By the action of chlorine on terchlorocarbolic acid dissolved in heavy hydrochloric ether (viii. 373), or on chlorisatin or bichlorisatin dissolved in alcohol. (Erdmann.)

*Preparation.* Chlorisatin or bichlorisatin is treated with chlorine gas in the manner described for the preparation of chloranil (p. 195), and the resinous mixture which remains after obtaining the chloranil from the lower oily liquid and evaporating the oil (and if distilled, would yield long needles of chlorinated chlorindoptene [quintichlorocarbolic acid contaminated with terchloraniline]), united with the perfectly similar

resinous mixture precipitated by boiling the upper liquid with water. Both these mixtures are dissolved, with the aid of heat, in potash; the prisms of impure quintichlorocarbolate of potash, which form on cooling, purified by recrystallisation from dilute potash, in which they are but sparingly soluble; and the acid separated in white flakes from the potash-salt by hydrochloric acid. (Erdmann.) — As Laurent, by nearly the same process, obtained brownish flakes, he boiled their solution in ammonia with a large quantity of water, till the excess of ammonia was expelled and a brown oil separated out; dissolved the laminæ obtained on cooling (whereas the mother-liquor yielded needles of terchlorocarbolic acid) in water; precipitated them from the solution by hydrochloric acid; and finally purified the still somewhat coloured acid by distillation.

*Properties.* Crystallises, best from rock-oil, in white right rhombic prisms truncated on the acute lateral edges. $u : u$ about $= 110°$. Less fusible than terchlorocarbolic acid. (Laurent.) Also less volatile; but when distilled with water, it sublimes in the neck of the retort in long needles. Smells like terchlorocarbolic acid, but more agreeably. — (Erdmann.)

| | | | Laurent. |
|---|---|---|---|
| 12 C | 72 | 27·07 | 27·8 |
| 5 Cl | 177 | 66·54 | 65·7 |
| H | 1 | 0·37 | 0·6 |
| 2 O | 16 | 6·02 | 5·9 |
| $C^{12}Cl^5HO^2$ | 266 | 100·00 | 100·0 |

*Quintichlorocarbolate of Ammonia.* — Aggregated needles very sparingly soluble in water. (Laurent.)

*Quintichlorocarbolate of Potash.* — Rhombic prisms and needles. (Erdmann.)

The potash-salt does not precipitate the salts of *lime* or *magnesia;* it precipitates *chloride of barium* in white flakes; *neutral acetate of lead,* white ; *ferrous* and *ferric* salts, brownish white; nitrate of *cobalt,* reddish; nitrate of *nickel,* greenish; *cupric sulphate,* dark purple violet; *mercurous* nitrate, in white flakes; *mercuric* chloride, in yellowish white flakes; nitrate of *silver,* lemon-yellow. (Erdmann.)

| | *Silver precipitate.* | | Erdmann (at 110°). |
|---|---|---|---|
| 12 C | 72 | 19·41 | 20·10 |
| 5 Cl | 177 | 47·71 | 46·81 |
| Ag | 108 | 28·57 | 31·41 |
| 2 O | 16 | 4·31 | 1·68 |
| $C^{12}Cl^5AgO^2$ | 373 | 100·00 | 100·00 |

*Oxychlorine-nucleus* $C^{12}ClH^3O^2$.

## Chlorkinone.

$C^{12}ClH^3O^4 = C^{12}ClH^3O^2,O^2$.

STÄDLER. (1849.) *Ann. Pharm.* 69, 300.

*Quinone monochlorée.*

*Preparation.* 1 pt. of kinate of copper or any other kinate (25 grammes at most) is distilled with 4 pts. of a mixture of 3 pts. common salt, 2 pts. peroxide of manganese, and 4 pts. oil of vitriol (diluted with 3 times its bulk of water), in a flask provided with a descending tube 6 ft. long, and kept cool at the upper part by a wet cloth, but not so much as to cause the liquid which distils over to crystallise. At first the mixture froths up considerably, giving off carbonic acid with a small quantity of chlorine, but when the liquid begins to boil, the evolution of chlorine ceases; the rapid ebullition is kept up, as long as any oil passes into the receiver from the tube, in which, if it be moderately cooled, all the chloranil is deposited. This oil, which solidifies on cooling, is collected on a filter, repeatedly washed with cold water, dried, pulverised and exhausted with successive small quantities of cold 85 p.c. alcohol, as long as the alcohol acquires a yellow colour and gives a precipitate with water. Bichlorkinone then remains undissolved, together with a small quantity of terchlorkinone and chloranil, whilst the alcohol retains in solution the kinone and terchlorkinone, which colour it yellow. These compounds are precipitated from the solution, by addition of a treble volume of water, in slender needles and laminæ, and dissolved in a small quantity of hot, moderately strong alcohol; the solution cooled, till the large yellow laminæ of terchlorkinone which separate out, begin to be associated with needles of chlorkinone; the liquid then immediately filtered and mixed with water; and the precipitate consisting of chlorkinone and a small quantity of terchlorkinone, freed from the latter by repeatedly treating it as above with alcohol, which however cannot be effected completely and is attended with great loss.

*Properties.* Very soft yellow needles, which melt at 100°, forming a dark yellow oil having a peculiar aromatic odour and sharp burning taste; its solution imparts a purple colour to the skin and other organic substances. Neutral.

| | | | Städeler. |
|---|---|---|---|
| 12 C | 72·0 | 50·56 | 39·48 |
| Cl | 35·4 | 24·86 | 41·31 |
| 3 H | 3·0 | 2·11 | 1·15 |
| 4 O | 32·0 | 22·47 | 18·06 |
| $C^{12}ClH^3O^4$ | 142·4 | 100·00 | 100·00 |

The above analysis gives nearly the formula of bichlorkinone or of a compound of chlorkinone and terchlorkinone in equal numbers of atoms; but the laminæ which occurred so abundantly in the substance analysed, showed clearly that it was a mere mixture of chlorkinone and terchlorkinone.

*Decompositions.* 1. The aqueous solution when boiled, becomes dark red and opaque, with formation of brown chlorkinhydrone ($C^{24}Cl^2H^8O^8$) and a brown resin.— 2. The reddish yellow solution in cold oil of vitriol quickly solidifies into a magma of white needles. — 3. Chlorkinone dissolves very readily in cold aqueous sulphurous acid, as chlorhydrokinone:

$$C^{12}ClH^3O^4 + 2SO^2 + 2HO = C^{12}ClH^5O^4 + 2SO^3.$$

*Combinations.* Chlorkinone dissolves in boiling *water* and separates on cooling.

It dissolves in *ether* and in strong *alcohol.* Also in a hot mixture of strong alcohol with an equal quantity of water; but on cooling, part of it separates out, and the portion which remains dissolved, changes the yellow colour of the solution by decomposition into wine-red.

With strong and weak *acetic acid,* it behaves in the same manner as with strong and weak alcohol. (Städeler.)

## Chlorhydrokinone.

$$C^{12}ClH^5O^4 = C^{12}ClH^3O^2,H^2O^2.$$

WÖHLER. (1845.) *Ann. Pharm.* 51, 155.
STÄDELER. *Ann. Pharm.* 69, 306.

*Colourless Chlorhydrokinone, Hydroquinone monochlorée.*

*Formation and Preparation.* 1. The solution of kinone in strong hydrochloric acid, after it has become colourless, is evaporated till it crystallises. The brown colour which the solution sometimes acquires during the evaporation, is likewise imparted to the crystals. (Wöhler.)—2. By dissolving chlorkinone in aqueous sulphurous acid. Since however chlorkinone, as hitherto obtained, always contains terchlorkinone, the process likewise yields terchlorhydrokinone. (Städeler.)

*Properties.* Colourless needles united in radiated groups, which melt very easily and solidify in the crystalline form on cooling; sublime at a somewhat stronger heat, in shining laminæ, and with partial carbonisation; have a faint peculiar odour, and sweetish, burning taste.

| | | | Wöhler. | Schnedermann. |
|---|---|---|---|---|
| 12 C | 72·0 | 49·87 | 50·21 | 50·42 |
| Cl | 35·4 | 24·51 | 24·31 | 23·82 |
| 5 H | 5·0 | 3·46 | 3·61 | 3·60 |
| 4 O | 32·0 | 22·16 | 21·87 | 22·16 |
| $C^{12}ClH^5O^4$ | 144·4 | 100·00 | 100·00 | 100·00 |

*Decompositions.* 1. Its aqueous solution immediately reduces silver from the solution of the nitrate, in specula and spangles, with emission of the odour of kinone (or of chlorkinone? according to the following equation: $C^{12}ClH^5O^4 + 2(AgO,NO^5) = C^{12}ClH^3O^4 + 2Ag + 2HO + 2NO^5$). (Laurent.)—2. The aqueous solution mixed with sesquichloride of iron, assumes a dark brown-red colour, becomes milky, and deposits dark brown oil-drops, which soon change to blackish green prisms ($2C^{12}ClH^5O^4 + 2Cl = C^{24}Cl^2H^8O^8 + 2HCl$. Laurent, *Compt. Chim.* 1849, 190.)—3. The deep blue solution of chlorhydrokinone in ammonia quickly turns green, then yellow, and lastly brown-red. (Wöhler.)

*Combinations.* It dissolves very readily in *water, alcohol* and *ether,* in the vapour of which it deliquesces. (Wöhler.)

*Conjugated Compound.*

## Chorkinhydrone.

$$C^{24}Cl^2H^8O^8 = C^{12}ClH^3O^4,C^{12}ClH^5O^4.$$

STÄDELER. *Ann. Pharm.* 69, 307.

*Brown Chlorhydrokinone.*

*Formation.* 1. By digesting aqueous chlorhydrokinone with chlorkinone:

$$C^{12}ClH^5O^4 + C^{12}ClH^3O^4 = C^{24}Cl^2H^8O^8.$$

2. By mixing aqueous chlorhydrokinone with sesquichloride of iron; as shown by Wöhler (*sup.*) — 3. By continued boiling of chlorkinone with a small quantity of water. (p. 186.) — 4. By the first action of strong hydrochloric acid upon kinone. (p. 160.)

Chlorkinhydrone is an oil, which, after some time, solidifies into a greenish brown crystalline mass: and this, when kept (in a sealed tube) sublimes in delicate brown needles, which impart a deep purple colour to the skin; it is decolorised by oil of vitriol, and appears therefore to contain water.

It reddens litmus, and forms a white precipitate with an alcoholic solution of neutral acetate of lead. (Städeler.)

*Oxychlorine-nucleus* $C^{12}Cl^2H^2O^2$.

## Bichlorkinone.

$$C^{12}Cl^2H^2O^4 = C^{12}Cl^2H^2O^2,O^2.$$

STÄDELER. (1849.) *Ann. Pharm.* 69, 309.

*Preparation.* From the mass obtained by distilling a salt of kinic acid with a chlorine-mixture, (p. 186) the chlorkinone and the greater part of the terchlorkinone are extracted by cold alcohol, then the rest of the terchlorkinone by hot alcohol mixed with an equal volume of water; the remaining mixture of bichlorkinone and a small quantity of chloranil dissolved in hot alcohol; and the crystals of bichlorkinone, after cooling, freed by elutriation of the mother-liquor from the delicate needles of chloranil, and purified by crystallisation from a mixture of ether and alcohol.

*Properties.* Dark yellow (lemon-yellow when crystallised from alcohol alone) glassy, oblique rhombic prisms, having their terminal faces obliquely set upon the obtuse lateral edges. Melts at 150°, becomes each time darker in colour, and volatilises slightly on exposure to the

air, more when boiled with water. Has a faint aromatic odour and is nearly tasteless. Its solution is neutral and does not colour the skin.

| | | | Städeler. |
|---|---|---|---|
| 12 C | 72·0 | 40·73 | 40·72 |
| 2 Cl | 70·8 | 40·04 | 40·14 |
| 2 H | 2·0 | 1·13 | 1·15 |
| 4 O | 32·0 | 18·10 | 17·99 |
| $C^{12}Cl^2H^2O^4$ | 176·8 | 100·00 | 100·00 |

*Decompositions.* Its deep red-brown solution in weak potash, deposits, after a few hours, slender red prisms of a potash-salt, from whose wine-red aqueous solution, hydrochloric acid throws down an acid (not further examined) resembling chloranilic acid and likewise forming red prisms. It dissolves sparingly in ammonia, forming a yellow solution which changes to red and then to black-brown; and if then evaporated, leaves sal-ammoniac and a brown substance, which yields a copious brown precipitate with hydrochloric acid.— When it is boiled with water, part of it volatilises undecomposed, and the remaining portion colours the water violet by decomposition. — By boiling with aqueous sulphurous acid, bichlorkinone is converted into bichlorkinhydrone and bichlorhydrokinone :

$$2C^{12}Cl^2H^2O^4 + 2SO^2 + 2HO = C^{24}Cl^4H^6O^8 + 2SO^3;$$

and :

$$C^{12}Cl^2H^2O^4 + 2SO^2 + 2HO = C^{12}Cl^2H^4O^4 + 2SO^3.$$

*Combinations.* Bichlorkinone is insoluble in *water*.

It dissoves in *oil of vitriol* without decomposition, forming a yellow solution from which it crystallises as it gradually absorbs water.

It dissolves without decomposition in strong boiling *hydrochloric acid*, and crystallises out on cooling.

It dissolves sparingly in cold, abundantly in hot *nitric acid* of sp. gr. 1·25, forming a yellow solution from which it crystallises undecomposed on cooling.

It dissolves readily and with yellow colour in *ether*.

It is nearly insoluble in cold strong *alcohol*, but dissolves abundantly in the same liquid at the boiling heat, forming a yellow solution from which it separates for the most part on cooling; the mother-liquor, after a few days, assumes. a dark brownish green colour, and then on addition of water becomes red. In spirit of 40 per cent. it dissolves but very sparingly, even on boiling.

It dissolves pretty freely in strong boiling *acetic acid*, separates therefrom on cooling in long prisms, and leaves a mother-liquor which soon becomes brown-red by decomposition. (Städeler,)

## Bichlorhydrokinone.

$$C^{12}Cl^2H^4O^4 = C^{12}Cl^2H^2O^2,H^2O^2.$$

STÄDELER. (1849.) *Ann. Pharm.* 69, 312.

*Colourless Bichlorhydrokinone.*

The colourless solution (*vid. sup.*) obtained by heating bichlorkinone with concentrated sulphurous acid, deposits on cooling, prisms which must be washed with cold water and dried.

Colourless needles and shorter prisms, resembling oxalic acid, having a pearly lustre, and united in stellate groups. Melts at 105°, forming a red-brown liquid, which solidifies again without colour on cooling. Sublimes at 120° in delicate needles, at 160°, very quickly, and when heated in contact with the air, diffuses white aromatic vapours. Has a burning aromatic taste. Reddens litmus.

| | | | Städeler. |
|---|---|---|---|
| 12 C | 72·0 | 40·27 | 40·24 |
| 2 Cl | 70·8 | 39·60 | |
| 4 H | 4·0 | 2·24 | 2·25 |
| 4 O | 32·0 | 17·89 | |
| $C^{12}Cl^2H^4O^4$ | 178·8 | 100·00 | |

*Decompositions.* 1. When set on fire, it burns with a very bright, green-edged flame.— 2. When immersed in nitric acid, it is immediately converted into bichlorkinone. Similarly, when its hot aqueous solution is mixed with a sufficient quantity of sesquichloride of iron, whereas a smaller quantity throws down violet or greenish black crystals of hydrated bichlorkinhydrone. [$C^{24}Cl^4H^6O^8 + 4Aq.$] Its solution in weak alcohol added to a neutral solution of nitrate of silver, precipitates, slowly at ordinary temperatures, more quickly at the boiling heat, a silver speculum, and yellow anhydrous, together with violet hydrated bichlorkinhydrone, but it does not part with a greater quantity of hydrogen.— 3. Its colourless solution in weak potash turns green and afterwards red on exposure to the air, and soon deposits a violet powder.— 4. Its yellow solution in ammonia becomes deep red on exposure to the air, and then yields a brownish deposit containing a crystalline and an amorphous substance.

*Combinations.* It dissolves very sparingly in cold, readily in hot *water.*

It is insoluble in cold, but dissolves in warm *oil of vitriol,* and crystallises therefrom on cooling, especially if the oil of vitriol can abstract water from it.

It dissolves sparingly in boiling *hydrochloric acid,* and separates on cooling.

It dissolves in *ammonia* with yellow colour, and in *potash* without colour.

It forms a white precipitate with neutral lead-acetate dissolved in alcohol.

It dissolves very readily in *alcohol, ether,* and warm *acetic acid.*

## Chloranilic Acid.

$C^{12}Cl^2H^2O^8 = C^{12}Cl^2H^2O^2,O^6$.

ERDMANN. (1841.) *J. pr. Chem.* 22, 281.

*Formation and Preparation.* The purple solution of chloranil in warm dilute potash (p. 197), deposits on cooling, nearly all the chlorani-

late of potash that has formed in it; this salt is then separated from the nearly decolorised mother-liquor (containing chloride of potassium and potash), and purified by recrystallisation from water. The cold aqueous solution of these crystals assumes a reddish yellow colour on addition of hydrochloric or sulphuric (not of acetic) acid; and soon afterwards deposits the chloranilic acid in reddish-white, micaceous scales, which, when collected on a filter, exhibit the colour of red lead. When the aqueous solution of chloranilate of potash is heated with an excess of the precipitating acid, the chloranilic acid is deposited on cooling in granules and laminæ.

*Properties.* Minium-coloured scales, granules or laminæ, which sublime but partially when heated in a test-tube, the greater part turning brown and decomposing.

| At 120°. | | | | | Erdmann. |
|---|---|---|---|---|---|
| 12 C | 72·0 | .... | 34·48 | .... | 35·08 |
| 2 Cl | 70·8 | .... | 33·91 | .... | 33·48 |
| 2 H | 2·0 | .... | 0·96 | .... | 1·05 |
| 8 O | 64·0 | .... | 30·65 | .... | 30·39 |
| $C^{12}Cl^2H^2O^8$ | 208·8 | .... | 100·00 | .... | 100·00 |

*Decomposition.* The violet solution of the acid in water is decolorised by nitric acid, with evolution of a colourless gas.

*Combinations.* The crystallised acid contains 7·14 p.c. (2 At.) *water*, which escape at 120°.—It dissolves with violet colour in water, and is precipitated therefrom by hydrochloric or sulphuric acid, with decoloration of the water.

*Chloranilate of Ammonia.*—The solution of the acid in warm ammonia yields crystals on cooling, which resemble the potash-salt in appearance and in their chemical relations.

*Chloranilate of Potash.*—*Preparation as above.* Brownish purple prisms having a strong lustre. They do not give off water at 100°, but burn at a higher temperature, with slight detonation and emission of purple vapours. (In dilute hydrochloric acid, they assume a red-lead colour without alteration of form: *Hofmann.*) They dissolve to a moderate amount in water and alcohol, forming violet-purple solutions; and to a smaller amount in aqueous potash.

| *Crystals.* | | | | | Erdmann. |
|---|---|---|---|---|---|
| 12 C | 72·0 | .... | 23·75 | ........ | 24·06 |
| 2 Cl | 70·8 | .... | 23·35 | | |
| 2 H | 2·0 | .... | 0·66 | ........ | 0·89 |
| 2 KO | 94·4 | .... | 31·13 | ........ | 30·77 |
| 8 O | 64·0 | .... | 21·11 | | |
| $C^{12}Cl^2K^2O^8 + 2Aq$ | 303·2 | .... | 100·00 | | |

The aqueous solution of the potash-salt precipitates *chloride of barium* in red-brown micaceous scales very sparingly soluble in boiling-water;—with *neutral acetate of lead* it forms a brown precipitate;—with *ferric* nitrate, blackish;—with *cupric* sulphate, greenish brown;—with *mercurous* nitrate, yellowish brown; and with nitrate of *silver*, a red-brown

pulverulent precipitate, which dissolves very sparingly and with reddish colour in water. It does not precipitate the protosalts of iron, cobalt or nickel, or corrosive sublimate. (Erdmann.)

| | *Silver-precipitate.* | | Erdmann. |
|---|---|---|---|
| 12 C | 72·0 | 17·03 | 17·40 |
| 2 Cl | 70·8 | 16·74 | 16·64 |
| 2 Ag | 216·0 | 51·09 | 51·06 |
| 8 O | 64·0 | 15·14 | 14·90 |
| $C^{12}Cl^{2}Ag^{2}O^{8}$ | 422·8 | 100·00 | 100·00 |

*Conjugated Compound.*

## Bichlorkinhydrone.

$$C^{24}Cl^{4}H^{6}O^{8} = Cl^{12}CH^{2}O^{4},C^{12}Cl^{2}H^{4}O^{4}.$$

STÄDELER. (1849.) *Ann. Pharm.* 69, 314.

*Coloured Bichlorhydrokinone.*

Obtained in the hydrated state by digesting aqueous bichlorhydrokinone with bichlorkinone, or with the proper quantity of sesquichloride of iron (if too little is used, bichlorhydrokinone remains unaltered; and with too much, bichlorkinone is formed), washing with cold water the crystals produced from the brown mixture on cooling, and drying them. These crystals may be freed from water at 70° or above, without losing their form.

*Properties.* Crystalline, yellow in the cold, becoming red every time it is heated above 110°. Has a faint odour like that of bichlorkinone, and an aromatic burning taste.

| | | | Städeler. |
|---|---|---|---|
| 24 C | 144·0 | 40·50 | 40·59 |
| 4 Cl | 141·6 | 39·82 | |
| 6 H | 6·0 | 1·69 | 1·91 |
| 8 O | 64·0 | 17·99 | |
| $C^{24}Cl^{4}H^{6}O^{8}$ | 356·6 | 100·00 | |

*Decompositions.* 1. Bichlorkinhydrone melts to a red liquid at 120°, and at the same time sublimes in isolated crystals of bichlorkinone and bichlorhydrokinone. — 2. It is not altered by cold dilute nitric acid, but moderately strong nitric acid converts it into bichlorkinone. — 3. Its solutions are turned green by hypochlorite of soda. — 4. Its chrome-green solution in dilute potash quickly changes to ruby-red, but is then no longer precipitated by hydrochloric acid; whereas the ammoniacal solution, which, in other respects, behaves in the same manner, forms with hydrochloric acid, a pale cochineal-coloured precipitate.

*Combinations. Hydrated Bichlorkinhydrone.* *Preparation, vid. sup.*— Ordinarily, small dark violet prisms united in stars; but when prepared

by mixing a hot aqueous solution of bichlorhydrokinone with sesquichloride of iron, it forms long flat blackish green needles like kinhydrone. The crystals, placed over oil of vitriol, or heated to 70°, give off their water, without change of form, and leaves the anhydrous yellow compound. Under oil of vitriol or a small quantity of alcohol, they also give off water and turn yellow.

| | | | Städeler. |
|---|---|---|---|
| 24 C | 144·0 | 36·77 | 36·90 |
| 4 Cl | 141·6 | 36·16 | |
| 10 H | 10·0 | 2·55 | 2·75 |
| 12 O | 96·0 | 24·52 | |
| $C^{24}Cl^4H^6O^8 + 4Aq$ | 391·6 | 100·00 | |

Or:

| | | | Städeler. |
|---|---|---|---|
| $C^{24}Cl^4H^6O^8$ | 355·6 | 90·81 | 90·91 |
| 4 HO | 36·0 | 9·19 | 9·09 |
| | 391·6 | 100·00 | 100·00 |

Bichlorkinhydrone is scarcely soluble in cold *water*, but dissolves readily in boiling water, whence it separates on cooling, partly as the yellow anhydrous compound, partly as the violet hydrate.

It dissolves with yellow colour in oil of vitriol, and crystallises out, also with yellow colour, as the oil of vitriol gradually takes up water.

It dissolves with chrome-green colour in aqueous *ammonia* or *potash*.

It dissolves readily and with yellow colour in *alcohol*.

It dissolves very readily in *ether*. The solution yields by spontaneous evaporation, partly yellow, partly violet crystals.

From the deep red solution in hot strong *acetic acid*, it crystallises on cooling in thin dark green prisms. (Städeler.)

*Oxychlorine-nucleus* $C^{12}Cl^3HO^2$.

## Terchlorkinone.

$C^{12}Cl^3HO^4 = C^{12}Cl^3HO^2,O^2$.

Woskressensky. (1839.) *J. pr. Chem.* 18, 419.
Städeler. *Ann. Pharm.* 69, 318.

*Trichlorchinon.*

*Formation.* By the action of chlorine upon kinone.

*Preparation.* 1. Dry chlorine gas is made to act upon kinone, which, in order that the temperature may not rise too high, must not be in large quantity, and must at first be cooled from without, but afterwards, to complete the decomposition, must be surrounded with hot water; the

resulting terchlorkinone, partly carried forward by the chlorine-gas, and partly sublimed in yellowish laminæ in the receiver, is then purified by solution in boiling alcohol and crystallisation, after addition of a small quantity of cold water. (Woskressensky.) —2. It is obtained in the preparation of chlorkinone (p. 186), and freed from that compound by repeated solution in hot moderately strong alcohol; as the solution cools, the terchlorkinone crystallises out first, and may then be washed with cold alcohol. The portion of terchlorkinone which dissolves together with the chlorkinone is precipitated by water, and further purified by alcohol, as above. (Städeler.)

*Properties.* Large golden-yellow laminæ. (Städeler.) Pale yellow, soft to the touch, friable. (Woskressensky.) Melts at 160° (somewhat above 100°, according to Woskressensky); and sublimes at 130° in delicate yellow iridescent laminæ. (Städeler.) Has a penetrating aromatic odour (Woskressensky); nearly inodorous, and at first tasteless, but afterwards produces an unpleasant scratching sensation in the throat. (Städeler.) The alcoholic solution does not redden litmus (Woskressensky), or colour the skin or other organic tissues, unless it contains a small quantity of chlorkinone, in which case it reddens them (Städeler); it imparts a dark red colour to organic substances. (Woskressensky.)

| | | | Woskressensky. | Städeler. |
|---|---|---|---|---|
| 12 C | 72·0 | 34·09 | 34·11 | 34·48 |
| 3 Cl | 106·2 | 50·29 | 49·45 | 50·10 |
| H | 1·0 | 0·47 | 0·79 | 0·54 |
| 4 O | 32·0 | 15·15 | 15·65 | 14·88 |
| $C^{12}Cl^{3}HO^{4}$ | 211·2 | 100·00 | 100·00 | 100·00 |

*Decompositions.* 1. When immersed in dilute potash, it turns green, then dissolves with red-brown colour, and after a few hours, deposits long red needles of a potash-salt, from whose wine-red aqueous solution, hydrochloric acid throws down red needles of the peculiar acid mentioned at page 189. (Städeler.) — 2. With ammoniacal gas it forms emerald-green crystals. (Woskressensky.) It dissolves after a while in weak ammonia, forming a red solution; with strong ammonia, it produces at first a green colour, but afterwards forms a brown-red solution, which when left to evaporate, forms small, hard, dark brown crystals. (Städeler.) — 3. By hot aqueous sulphurous acid, it is converted into terchlorhydrokinone. (Städeler.)

*Combinations.* It is soluble in cold, but dissolves very sparingly in boiling water. (Städeler.)

From its deep yellow solution in *cold oil of vitriol,* it is precipitated by water. (Städeler.)

From its solution in hot strong *nitric acid,* it crystallises in yellow laminæ on cooling. (Städeler.)

Its alcoholic solution does not precipitate *neutral acetate of lead* or nitrate of *silver.* (Woskressensky.)

It dissolves sparingly in cold, more abundantly in hot *alcohol,* and separates on cooling, the more completely as the alcohol is weaker. (Städeler.)

It dissolves in *ether*. (Woskressensky, Städeler.)

With *acetic acid*, both strong and weak, it behaves as with alcohol. (Städeler.)

## Terchlorhydrokinone.

$$C^{12}Cl^3H^3O^4 = C^{12}Cl^3HO^2,H^2O^2.$$

Städeler. (1849.) *Ann. Pharm.* 69, 321.

*Preparation.* The colourless solution of terchlorkinone in a sufficient quantity of hot aqueous sulphurous acid, deposits the terchlorhydrokinone, on cooling, in small crystals, or on evaporation over the water-bath in the form of a heavy oil which crystallises as it cools; a portion, however, remains in solution, and may be obtained by evaporating the aqueous solution in vacuo over oil of vitriol. It is freed from adhering sulphuric acid by washing with cold water.

*Properties.* Colourless laminæ and flat prisms, which melt somewhat above 130°, and sublime in delicate iridescent laminæ. Has a faint aromatic odour, and a burning aromatic taste, especially when moistened with alcohol. The alcoholic solution reddens litmus.

*Decompositions.* 1. Its solutions are coloured green by *hypochlorite of soda.* — 2. Strong (not dilute) *nitric acid,* converts it by oxidation into terchlorkinhydrone. The same compound appears to be formed on adding *nitrate of silver* to a weak alcoholic solution of terchlorhydrokinone, a specular deposit of silver being formed after some minutes (or more quickly if aided by heat), and afterwards yellow rhombic laminæ deposited,—or when to the same solution, *sesquichloride of iron* is added, which at first produces a deep brown colour. — 3. Its solution in aqueous potash or ammonia, which is colourless at first, turns green, red, and brown when exposed to the air, and afterwards, without depositing crystals, forms with hydrochloric acid a thick precipitate, which, when formed from the potash-solution, is converted by boiling into a heavy mixture of light yellow laminæ and black-blue crystals recognisable by the microscope, and when formed from the ammonia-salt appears flesh-coloured and amorphous.

*Combinations.* It dissolves sparingly in cold *water,* slowly and with fusion in boiling water, from which it separates partially on cooling.

From its solution in warm *oil of vitriol,* it crystallises as the liquid absorbs water.

Its alcoholic solution forms a white precipitate with *neutral acetate of lead.*

It dissolves readily in *alcohol* and *ether.*

*Conjugated Compound.*

## Terchlorkinhydrone.

$$C^{24}Cl^6H^4O^8 = C^{12}Cl^3HO^4,C^{12}Cl^3H^3O^4.$$

STÄDELER. (1849.) *Ann. Pharm.* 69, 323.

*Yellow Trichlorhydrochinone.*

When terchlorkinone is boiled with a quantity of aqueous sulphurous acid, less than sufficient to convert it into terchlorhydrokinone, a red-brown liquid is formed, on which there float brown viscid oil-drops, probably belonging to this compound; in a larger quantity of sulphurous acid, they dissolve without colour, as chlorhydrokinone.

*Chlorine-nucleus* $C^{12}Cl^4O^2$.

## Chloranil.

$$C^{12}Cl^4O^4 = C^{12}Cl^4O^2,O^2.$$

ERDMANN. (1849.) *J. pr. Chem.* 23, 273 and 279.
A. W. HOFMANN. *Ann. Pharm.* 52, 55.

*Formation.* 1. From carbolic acid, kinone (Hofmann), aniline (Fritzche), chloraniline, binitrocarbolic acid or ternitrocarbolic acid (Hofmann), when either of these compounds is heated with hydrochloric acid and chlorate of potash. — 2. Similarly from salicylous acid, salicylic acid (also, according to Cahours), nitrosalicylic acid, or anthranilic acid, with evolution of carbonic acid. (Not from benzoic acid or its allied compounds.) (Hofmann.)—3. From kinic acid when heated with common salt, peroxide of manganese, and sulphuric acid, — together with carbonic acid, the three chlorkinones, &c. (Städeler.) — 4. From isatin, when boiled with hydrochloric acid and chlorate of potash (Laurent); from alcoholic chlorisatin or bichlorisatin by the action of chlorine gas (Erdmann); or more quickly by hydrochloric acid and chlorate of potash, — whereas indigo treated in the same manner, gives only traces of this compound. (Hofmann.) — 5. From pyrocatechin, $C^{12}H^6O^4$, by the action of hydrochloric acid and chlorate of potash (R. Wagner, *J. pr. Chem.* 67, 441):

$$C^{12}H^6O^4 + 10Cl = C^{12}Cl^4O^4 + 6HCl.$$

*Preparation.* Strong hydrochloric acid is poured upon carbolic acid in a basin; chlorate of potash added in small crystals; and the mixture heated as soon as the first violent action, which may amount to explosion, is over, the heating being continued for some time, till in fact the

carbolic acid, which at first becomes thick and red-brown, is converted into a light yellow crystalline mass, which, after washing with water, may be crystallised from boiling alcohol. The transformation takes place more quickly when the carbolic acid is dissolved in boiling water or in alcohol; but if alcohol be used, it is necessary, on account of the readiness with which explosion takes place, to use more dilute hydrochloric acid and to add the chlorate of potash gradually. (Hofmann.) — 2. By boiling kinone (Hofmann), or the wash-water obtained in the preparation of kinone by Wöhler's process (p. 159), which contains kinone in the state of very dilute solution (Städeler), with hydrochloric acid and chlorate of potash. — 3. Similarly, binitrocarbolic or ternitrocarbolic acid dissolved in water or alcohol. (Hofmann.)— 4. Also salicylous acid, salicylic acid, nitrosalicylic acid, or salicin. The last must be dissolved, together with chlorate of potash, in boiling water, and small quantities of hydrochloric acid then added, whereupon the solution immediately acquires a deep orange-yellow colour, and becomes covered with a crust of small crystals of chloranil, amounting to 30·27 p.c. of the salicin. If the salicin be first heated with hydrochloric acid alone, saliretin is formed, which, when afterwards heated with chlorate of potash, does not yield any chloranil. (Hofmann.) — 5. When a salt of kinic acid is distilled with common salt, peroxide of manganese, and aqueous sulphuric acid (p. 186), a portion of the chloranil thereby produced sublimes in the upper part of the flask and in the distillation-tube, a considerable portion, however, remaining in the residue. (Städeler.) — 6. Chlorine gas is passed through 80 per cent. alcohol in which chlorisatin or bichlorisatin is dissolved or suspended, till the thick oily liquid which falls down no longer increases, and nothing more is formed than products of decomposition of the alcohol; the oily liquid, after removal of the sal-ammoniac by water, is exhausted with cold alcohol, which dissolves chlorinated chlorindoptene and a resinous substance, together with heavy hydrochloric ether and other products of decomposition of the alcohol, and leaves the greater part of the chloranil in the crystalline form. The alcoholic solution evaporated to a syrup and cooled yields an additional quantity of chloranil crystals to be purified by exhaustion with cold alcohol; and the alcoholic liquid thereby obtained, yields still an additional quantity by repetition of the process. The whole of the chloranil crystals are washed with water, and finally purified by repeated crystallisation from hot alcohol, or by sublimation—a small quantity of charcoal then remaining—and washing the sublimate with cold alcohol. (Erdmann.) — 7. Pulverised isatin is added to boiling hydrochloric acid, then chlorate of potash; and the resulting soft mass mixed with crystals, is washed with water, thrown upon a filter together with a little ether, washed with cold alcohol, and purified by crystallisation from hot alcohol, or by sublimation. (Laurent; *Rev. scient.* 19, 141; abstr. *J. pr. Chem.* 36, 277.)

*Properties.* Pale yellow (golden-yellow according to Hofmann), nacreous, often iridescent laminæ. (Erdmann.) Volatilises completely at a gentle heat without fusion, and without leaving any residue of charcoal (slowly at 150°, quickly between 210° and 220°: *Hofmann*), in yellow vapours, which condense on cold bodies in delicate laminæ, and on hot bodies in the form of a liquid, solidifying to a sulphur-yellow crystalline mass on cooling. Larger quantities of chloranil, when rapidly heated, melt partially into a dark brown boiling liquid, and leave a small

quantity of charcoal. — The alcoholic solution has no action on vegetable colours. (Erdmann.)

| | | | Erdmann. | | Hofmann. | Laurent. |
|---|---|---|---|---|---|---|
| | | | *From alcohol.* | *Sublimed.* | | |
| 12 C | 72·0 | 29·31 | 30·63 | 29·82 | 30·14 | 29·50 |
| 4 Cl | 141·6 | 57·66 | 57·60 | 57·74 | 56·20 | |
| 4 O | 32·0 | 13·03 | 11·77 | 12·44 | 13·32 | |
| H | | | | | 0·34 | |
| $C^{12}Cl^4O^4$ | 245·6 | 100·00 | 100·00 | 100·00 | 100·00 | |

*Decompositions.* 1. Chloranil dissolves very readily and with dark purple colour (after previously assuming a greenish black colour: *Hofmann*), in warm dilute *potash*, in the form of chloranilate of potash, which soon crystallises, and chloride of potassium.

$$C^{12}Cl^4O^4 + 4KO = C^{12}Cl^2K^2O^8 + 2KCl. \quad \text{(Erdmann.)}$$

When strong potash is used, part of the product is further decomposed, so that the brown-red solution yields but a small quantity of chloranilate of potash, and a dark mother-liquor which is not precipitated by hydrochloric acid. (Erdmann.) — 2. It dissolves slowly and with deep blood-red colour in aqueous ammonia, forming chloranilammone (chloranilamate of ammonia, according to Laurent) which crystallises out, and sal-ammoniac:

$$C^{12}Cl^4O^4 + 4NH^3 + 2HO = C^{12}N^2Cl^2H^6O^6 + 2NH^4Cl.$$

3. Chloranil gently heated with alcohol to which ammonia is added, yields brown-red chloranilamide which remains undissolved, together with a solution of chloranilamate of ammonia and another substance:

$$C^{12}Cl^4O^4 + 4NH^3 = C^{12}N^2Cl^2H^4O^4 + 2NH^4Cl.$$

If absolute alcohol and ammoniacal gas were used, the chief product would probably be chloranilamide. (Laurent.) — 4. The yellow solution of chloranil in aqueous monosulphide of potassium, quickly mixed with hydrochloric acid, without contact of air, yields a precipitate which has a sulphur-yellow colour when dry. This precipitate, when heated, yields a few colourless needles and laminæ, then melts and decomposes, giving off sulphurous acid. It dissolves in alcohol and ether, and with red-brown colour in potash. When purified from any free sulphur that may be mechanically mixed with it, by treating it with sulphide of carbon, whereby it is partially dissolved, it contains 8·1 p. c. sulphur and 51·8 chlorine. On exposure to the air, the yellow solution of chloranil in monosulphide of potassium, quickly turns red, then brown, then black, and deposits a black granular powder, which contains sulphur and potash, and does not dissolve in water or alcohol. The yellow solution of chloranil in ordinary liver of sulphur, becomes yellowish red on exposure to the air, then assumes a continually deeper purple, and at last a black colour, first depositing sulphur and afterwards a black powder. (Erdmann.) — 5. Chloranil boiled with aqueous sulphurous acid, takes up 2H and is converted into chlorhydranil. (Städeler.)

Chloranil is not decomposed by sulphuric, hydrochloric, or even by boiling nitric acid (or by boiling aqua-regia, or by chloride of lime: *Stenhouse*); neither is any decomposing action exerted upon it by an

alcoholic solution of iodide or bromide of potassium when boiled, or by cyanide of mercury when sublimed with it. (Erdmann.)

*Combinations.* Chloranil is insoluble in water. (Erdmann.)

It is nearly insoluble in cold *alcohol,* but dissolves sparingly in boiling alcohol, forming a yellow solution which changes to light violet on exposure to the air, and deposits nearly all the chloranil on cooling. (Hofmann.)

In *ether,* it dissolves somewhat more freely. (Hofmann.)

## Chlorhydranil.

$$C^{12}Cl^4H^2O^4 = C^{12}Cl^4O^2,H^2O^2.$$

STÄDELER. (1849.) *Ann. Pharm.* 69, 327.

*Formation and Preparation.* Crystals of chloranil are boiled with aqueous sulphurous acid till they exhibit no further change of colour; the then brownish white crystals collected on a filter, washed with cold water, and dissolved, after drying, in a mixture of ether and weak alcohol; the solution left to evaporate till it crystallises; the mass of brownish white laminæ dissolved in strong boiling acetic acid; and the solution filtered from a brownish tenacious mass, and cooled to the crystallising point.

*Properties.* Delicate white nacreous laminæ. They do not alter at 50° but become slightly brown at 160°, strongly between 215° and 220°; sublime rather quickly at that temperature, but do not melt till more strongly heated, and then solidify in a crystalline mass on cooling. Inodorous and tasteless. In solution it reddens litmus.

| | | | Städeler. |
|---|---|---|---|
| 12 C | 72·0 | 29·08 | 29·46 |
| 4 Cl | 141·6 | 57·19 | |
| 2 H | 2·0 | 0·81 | 0·90 |
| 4 O | 32·0 | 12·92 | |
| $C^{12}Cl^2H^2O^4$ | 247·6 | 100·00 | |

*Decompositions.* 1. By hypochlorite of soda, most readily when a small quantity of that salt is added by drops to its solution in a small quantity of alcohol, it is converted into needles of a deep green colour, which, when heated in a test-tube, give off chloranil and leave charcoal, and are soluble in water and in alcohol. — 2. When heated with water containing a small quantity of nitric acid or sesquichloride of iron, it turns yellow; also when its hot solution in weak alcohol is mixed with a hot solution of nitrate of silver, the silver being then deposited in the specular or pulverulent form; and the hot filtrate, on cooling, yields delicate rhombic laminæ, perhaps of $C^{12}Cl^4HO^4$ [or of chloranil ?]. — 3. Its hot-saturated solution in potash-ley deposits on cooling a considerable number of prisms of a potash salt, which, as well as its solution, quickly turns red on exposure to the air. — 4. Its yellow solution in

warm aqueous ammonia turns violet when mixed with hydrochloric acid, and forms with chloride of calcium, after a while, a crystalline precipitate which changes on exposure to the air. The same solution exposed to the air in a basin turns green from above downwards, then gradually deposits a green crystalline powder, and becomes red. — Chlorhydranil is neither decomposed nor dissolved by warm oil of vitriol

*Combinations.* — Chlorhydranil is insoluble in water.

It dissolves with yellow colour in aqueous *ammonia*, especially when heated, and readily and without colour in cold dilute potash, wherein it is precipitated in the crystalline form by hydrochloric acid.

Its alcoholic solution forms a white precipitate with *neutral acetate of lead.*

It dissolves readily in *alcohol* and in *ether.* (Städeler.)

¶ *Sulphochlorine-nucleus* $C^{12}ClH^4(SO^2)$.

## Chlorosulphobenzene.

$C^{12}ClH^4(SO^2)$.

H. Gericke. *Ann. Pharm.* 100, 213.

Formed by the action of chlorine on sulphobenzene.¶ Chlorine gas acts upon dry sulphobenzene, even in the cold, and especially in sunshine, forming the hydrochlorate of chlorosulphobenzene, contaminated however with undecomposed sulphobenzene. But by passing chlorine gas over melted sulphobenzene, the hydrochlorate of chlorosulphobenzene is obtained in a purer state and in yellow oily drops, which may be further purified by repeated solution in alcohol and precipitation by water This hydrochlorate, when suddenly heated, is resolved into hydrochloric acid and chlorosulphobenzene, which separates in the neck of the retort as a yellow crystalline mass. It is also separated by digesting the hydrochlorate with alcoholic potash, whereby a precipitate of chloride of potassium is formed, and the filtrate as it cools deposits crystals of chlorosulphobenzene, which may be purified by washing with water and recrystallisation from alcohol and ether.

Colourless crystalline mass, which, under the microscope, appears to be formed of long acuminated crystals. Melts at about 152°, and solidifies again in the crystalline form, but sublimes at temperatures much below its melting point. By repeated melting and cooling, the melting point sinks to 64°. It is decomposed by boiling with alcoholic potash, unaltered chlorosulphobenzene passing over at first with the alcohol-vapours, but afterwards sulphobenzene passes over in oily drops which solidify in the crystalline state, and charcoal remains in the retort. Chlorosulphobenzene is not reduced to sulphobenzene by the action of zinc and sulphuric acid. It is insoluble in water and in dilute acids, alkalis, and alkaline carbonates.

*Hydrochlorate of Chlorosulphobenzene.—Preparation* (vid. sup.). Yellow oily drops, heavier than water, having an odour like that of sulphite of

chlorobenzene (p. 174) and a disagreeable taste. Has no action upon litmus. Distils without decomposition at 150°.

| | | | Gericke. |
|---|---|---|---|
| 12 C | 72·0 | 40·0 | 40·2 |
| 5 H | 5·0 | 2·8 | 3·0 |
| 2 Cl | 70·8 | 39·4 | 37·2 |
| 2 S | 16·0 | 8·9 | |
| 2 O | 16·0 | 8·9 | |
| $C^{12}ClH^4(SO^2),HCl$ | 179·8 | 100·0 | |

Gericke doubles the formula of chlorosulphobenzene, making it $C^{24}Cl^2H^8(SO^2)^2$, and the hydrochlorate $C^{24}Cl^2H^8(SO^2)^2,2HCl$.

The hydrochlorate burns on platinum-foil, with a smoky flame and disagreeable odour. It is not decomposed or dissolved by dilute alkalis or by dilute sulphuric or hydrochloric acid. Nitric acid acts upon it with evolution of red vapours and probably forms a nitro-compound. Heated with iodide of potassium, it forms a blood-red liquid.

It is insoluble in water, but dissolves in *alcohol* and *ether*. When exposed to the air, it absorbs water and evaporates quickly. (Gericke.) ¶

*Nitro-nucleus* $C^{12}XH^5$.

## Nitrobenzene.

$C^{12}NH^5O^4 = C^{12}XH^5$.

MITSCHERLICH. (1834.) *Pogg.* 31, 625.

*Nitrobenzol, Nitrobenzin, Nitrobenzid, Nitrobenzinase, Nitrofune.*

*Formation.* 1. By heating benzene with fuming nitric acid. (Mitscherlich.)—2. By the dry distillation of nitrobenzoate of silver. (Mulder, *J. pr. Chem.* 19, 375.)

*Preparation.* Benzene is added by small portions to warm fuming nitric acid, and the nitrobenzene which separates on cooling washed with water. (Mitscherlich.) Hilkenkamp (*Ann. Pharm.* 95, 86) adds the benzene to cold fuming nitric acid.

*Properties.* Needles at 3°; above 3°, a yellowish liquid of sp. gr. 1·209 at 15°; boils at 213°. Vapour-density 4·4. Smells like bitter almond oil and cinnamon oil; tastes very sweet. (Mitscherlich.)

| | | | Mitscherlich. | Mulder. |
|---|---|---|---|---|
| 12 C | 72 | 58·54 | 58·53 | 58·35 |
| N | 14 | 11·38 | 11·70 | |
| 5 H | 5 | 4·06 | 4·08 | 4·07 |
| 4 O | 32 | 26·02 | 25·69 | |
| $C^{12}NH^5O^4$ | 123 | 100·00 | 100·00 | |

| | Vol. | | Density. |
|---|---|---|---|
| C-vapour | 12 | ........... | 4·9920 |
| N-gas | 1 | ........... | 0·9706 |
| H-gas | 5 | ........... | 0·3465 |
| O-gas | 2 | ........... | 2·2186 |
| Vapour of Nitrobenzene | 2 | ........... | 8·5277 |
| | 1 | ........... | 4·2638 |

*Decompositions.* Nitrobenzene passed in the state of vapour through a hot tube, together with chlorine gas, is decomposed, with formation of hydrochloric acid. (Mitscherlich.) — 2. By boiling with fuming nitric acid, it is converted into binitrobenzene. (Deville.) — 3. When heated with oil of vitriol it becomes strongly coloured and eliminates sulphurous acid gas. — It is not decomposed at ordinary temperatures by chlorine or bromine, or when heated with moderately strong nitric or dilute sulphuric acid. — 4. Nitrobenzene is but little affected by aqueous potash or ammonia at a boiling heat, or by lime when distilled over it; but with boiling alcoholic potash it forms a red liquid, which when distilled yields azobenzene $C^{24}N^2H^{10}$ in the form of a red liquid crystallising as it cools, whilst a peculiar potash-salt remains in the retort. (Mitscherlich.) In this process, aniline also distils over, and at a later stage a large quantity of oxalic acid is found in the residue. (Hofmann & Muspratt, *Ann Pharm.* 54, 27.) — The solution of 1 vol. nitrobenzene in 8 vol. strong alcohol boils, on addition of a quantity of hydrate of potash equal to that of the nitrobenzene, assuming at the same time a dark brown-red colour, and, after the boiling has been up for some minutes by external heating, deposits yellowish brown needles of azoxybenzene, $C^{24}N^2H^{10}O^2$, and, when the alcohol is distilled off, separates into two layers, the lower of which contains potash, carbonate of potash, a brown potash-salt easily soluble in water, nearly insoluble in alcohol (whereas the brown acid contained in it dissolves in alcohol but not in water), and an indifferent dark brown powder, sparingly soluble in water and alcohol, whilst the upper layer is a dark brown oil which, on cooling, gradually solidifies into needle-shaped azoxybenzene (amounting to half the nitrobenzene). This azoxybenzene when distilled, yields azobenzene, with a nearly equal quantity of aniline. (Zinin, *J. pr. Chem.* 36, 98.) Laurent & Gerhardt (*Compt. Chim.* 1849, 417; also *Ann. Pharm.* 75, 70) endeavoured to find a formula for this decomposition by alcoholic potash.—5. When sulphuretted hydrogen is passed through nitrobenzene dissolved in alcohol and mixed with ammonia, crystals of sulphur are deposited, the liquid loses the odour of sulphuretted hydrogen, and solidifies at 0° after some time into a mass of delicate yellow needles, which have a biting taste and dissolve readily in water and alcohol; this crystalline mass, when freed by distillation from part of the alcohol, continually deposits sulphur and ultimately leaves aniline. (Zinin.)

$$C^{12}NH^5O^4 + 6HS = C^{12}NH^7 + 4HO + 6S.$$

6. It is quickly converted into aniline when placed in contact with zinc and a mixture of alcohol and hydrochloric acid in equal volumes. (Hofmann, *Ann. Pharm.* 55, 201.)

$$C^{12}NH^5O^4 + 6H = C^{12}NH^7 + 4HO.$$

¶ 7. Aniline is also produced by the action of ferrous acetate upon nitrobenzene:

$$C^{12}NH^5O^4 + 12FeO + 2HO = 6Fe^2O^3 + C^{12}NH^7.$$

Ferrous sulphate, oxalate and hydrochlorate do not act upon nitrobenzene. When 1 pt. of nitrobenzene, $1\frac{1}{2}$ pt. iron filings, and 1 pt. concentrated acetic acid are introduced into a retort, a brisk action commences without external heating, and the distillate, which must be collected in a well-cooled receiver, consists of aniline, acetate of aniline, and undecomposed nitrobenzene :

$$C^{12}NH^5O^4 + 4Fe + 2HO = 2Fe^2O^3 + C^{12}NH^7.$$

On pouring the contents of the receiver into the retort after cooling, distilling to dryness, and treating the distillate with potash-ley, aqueous aniline separates out. (A. Béchamp, *N. Ann. Chim. Phys.* 42, 186.) — 8. Nitrobenzene heated to the boiling point for some hours with dry sulphite of ammonia and absolute alcohol, with addition of carbonate of ammonia to keep the liquid alkaline (otherwise the principal product is decomposed by the sulphurous acid evolved) yields, after the liquid has been left to cool, filtered from the sulphate of ammonia which separates out, and evaporated to an oily consistence, also with addition of carbonate of ammonia, — a large quantity of delicate white laminæ which quickly decompose, and a smaller quantity of fine hard needles consisting of the ammonia-salt of *dithiobenzolic* or *phenyldisulpho-diamic acid* [$C^{12}N^2H^8S^4O^{12} = C^{12}Ad^2H^4S^4O^{12}$], the formation of which appears to be due to the action of the sulphite of ammonia on binitrobenzene $C^{12}(NO^4)^2H^4$, contained in the nitrobenzene.

$$C^{12}(NO^4)^2H^4 + 12(NH^4O,SO^2) = C^{12}Ad^2H^2(NH^4)^2,S^4O^{12} + 8(NH^4O,SO^3) + 2NH^3.$$

The laminæ probably consists of the ammonia-salt of *thiobenzolic, phenyl-disulphamic*, or *disulphanilic acid* [$C^{12}AdH^5S^2O^6$], formed by the action of sulphite of ammonia on the nitrobenzene itself.

$$[C^{12}(NO^4)H^5 + 6(NH^4O,SO^2) = C^{12}AdH^4(NH^4),S^2O^6 + 4(NH^4O,SO^3) + NH^3.]$$

(L. Hilkenkamp, *Ann. Pharm.* 95, 86; *Chem. Gaz.* 1855, 461.) ¶.

*Combinations.* Nitrobenzene is insoluble in water.

It dissolves readily in strong *sulphuric* or *nitric acid*, especially when heated.

It mixes in all proportions with *alcohol* and *ether*. (Mitscherlich.)

## Nitrocarbolic Acid.

$$C^{12}NH^5O^6 = C^{12}XH^5,O^2.$$

*Mononitrophenol, einfach-Nitrophenol, Nitrocarbolsäure.*

*Formation.* 1. By treating carbolic acid with nitric acid. — 2. By treating aniline with nitric acid and arsenious acid. — 3. By passing nitric oxide through a solution of aniline in rather strong nitric acid, a brown resinous mixture is obtained, consisting of crystalline nitrocarbolic acid with a brown amorphous substance and a trace of carbolic acid. — Nitrocarbolic acid is a beautiful crystalline body. (A. W. Hofmann, *Ann. Pharm.* 75, 358.)

*Nitrochlorine-nucleus* $C^{12}XClH^4$.

## Nitrochloroniceic Acid.

$C^{12}NClH^4O^8 = C^{12}XClH^4,O^4$.

St. Evre. (1849.) *N. Ann. Chim. Phys.* 25, 492; also *Ann. Pharm.* 70, 261.

*Acidé chloronicéique nitré, Nitrochloronicensäure.*

Crystallises on cooling from a solution of chloroniceic acid in fuming nitric acid and is purified by crystallisation from alcohol.

Broad micaceous laminæ having a fatty lustre.

| | | | St. Evre. |
|---|---|---|---|
| 12 C | 72·0 | 38·02 | 37·83 |
| N | 14·0 | 7·39 | 7·77 |
| Cl | 35·4 | 18·69 | 18·35 |
| 4 H | 4·0 | 2·11 | 2·25 |
| 8 O | 64·0 | 33·79 | 33·80 |
| $C^{12}NClH^4O^8$ | 189·4 | 100·00 | 100·00 |

## Nitrochloroniceic Ether.

$C^{16}NClH^8O^8 = C^4H^5O,C^{12}XClH^3O^3$.

Broad colourless laminæ. (St. Evre.)

| | | | St. Evre. |
|---|---|---|---|
| 16 C | 96·0 | 44·16 | 43·75 |
| N | 14·0 | 6·44 | 6·69 |
| Cl | 35·4 | 16·28 | 15·78 |
| 8 H | 68·0 | 3·68 | 3·74 |
| 8 O | 64·0 | 29·44 | 30·04 |
| $C^{16}NClH^8O^8$ | 217·4 | 100·00 | 100·00 |

*Nitro-nucleus* $C^{12}X^2H^4$.

## Binitrobenzene.

$C^{12}N^2H^4O^8 = C^{12}X^2H^4$.

Deville. (1841.) *N. Ann. Chim. Phys.* 3, 187; also *J. pr. Chem.* 25, 353.

Muspratt & A. W. Hofmann. *Phil. Mag. J.* 29, 318; also *Ann. Pharm.* 57, 214.

*Binitrobenzol, Dinitrobenzol, Binitrobenzide, Nitrobenzinèse.*

*Preparation.* A solution of 1 pt. nitrobenzene in 6 pts. fuming nitric acid is boiled down to 1·4 pt., the acid removed from the residue by washing with water and then crystallised from alcohol. (Deville.) — 2. Benzene or nitrobenzene is dropt, as long as it dissolves, into a mixture of equal parts of fuming nitric acid and oil of vitriol; the solution boiled for some minutes; and the crystalline magma which forms on cooling, washed with water, and left to crystallise from alcohol. (Hofmann & Muspratt.)

*Properties.* Long shining needles and laminæ which melt below 100°, and solidify in a radiated mass on cooling. (Deville.)

| | | | Deville. | Hofmann & Muspratt. |
|---|---|---|---|---|
| 12 C | 72 | 42·86 | 42·70 | 43·26 |
| 2 N | 28 | 16·66 | 17·10 | |
| 4 H | 4 | 2·38 | 2·56 | 3·42 |
| 8 O | 64 | 38·10 | 37·64 | |
| $C^{12}N^2H^4O^8$ | 168 | 100·00 | 100·00 | |

Binitrobenzene boiled with sulphite of ammonia and absolute alcohol is converted into dithiobenzolate of ammonia. (Hilkenkamp, see p. 203.)

It dissolves very readily in hot alcohol. (Deville.)

## Binitrocarbolic Acid.

$$C^{12}N^2H^4O^{10} = C^{12}X^2H^4,O^2.$$

LAURENT. (1841.) *N. Ann. Chim. Phys.* 3, 213; also *Ann. Pharm.* 43, 213; also *J. pr. Chem.* 25, 416.

*Binitrocarbolsäure, Nitrophänessaure, Acide nitrophénesique,*

*Formation.* 1. By the more moderate action of nitric acid upon carbolic acid. (Laurent):

$$C^{12}H^6O^2 + 2NO^5 = C^{12}N^2H^4O^{10} + 2HO.$$

2. By boiling binitranisol ($C^{14}X^2H^6O^{10}$) with alcoholic potash. (Cahours, *N. Ann. Chim. Phys.* 25, 22.)

*Preparation.* 12 pts. of commercial nitric acid are added by separate portions in a large porcelain basin to 1 pt. of that portion of coal-tar oil which boils between 160° and 190°, a fresh portion being added as soon as the violent intumescence caused by the preceding has subsided, in which case the mixture becomes hot enough to render external heating unnecessary. The resulting thick red-brown mass is freed by water from the greater part of the nitric acid; the residue boiled with very dilute ammonia; the solution while hot rapidly filtered from a brown resinous mass which serves for the preparation of picric acid; the brown crystalline substance which separates within 24 hours from the dark brown filtrate, collected (an additional quantity of the brown resinous mass

serving for the preparation of picric acid, may be precipitated from the mother-liquor by acids); the crystalline substance dissolved in boiling water; the delicate needles of binitrocarbolate of ammonia which form on cooling, purified by four recrystallisations (the matter precipitated from the mother-liquors by nitric acid serves for the preparation of picric acid), washed with cold water, and dissolved in a very large quantity of boiling water; the solution filtered as quickly as possible from any of the brown mass that may be precipitated; the mother-liquor decanted from the acid which crystallises on cooling, boiled with fresh ammonia, again mixed with nitric acid &c., and finally, the acid, which is thus obtained crystallised in fork-like tufts, is dissolved in boiling alcohol to purify it from a small quantity of oil: it then crystallises free from oil on cooling. (Laurent.)

*Properties.* Pale brown yellow prisms belonging to the right prismatic system. Fig. 56, $u:t=115°$; $i:t=127°$; $u:u=50°$ and $130°$ (*Rev. scient.* 9, 24). Melts at 114°, and solidifies in a radiated mass on cooling. May be distilled in small quantities without decomposition. Inodorous; tasteless at first, afterwards very bitter. Colours the cuticle, horn, and other animal tissues, deep yellow. (Laurent.)

| | | | Laurent. | Cahours. |
|---|---|---|---|---|
| 12 C | 72 | 39·13 | 39·35 | 39·18 |
| 2 N | 28 | 15·22 | 15·76 | 15·21 |
| 4 H | 4 | 2·17 | 2·28 | 2·17 |
| 10 O | 80 | 43·48 | 42·61 | 43·44 |
| $C^{12}X^2H^4O^2$ | 184 | 100·00 | 100·00 | 100·00 |

*Decompositions.* 1. The acid detonates when suddenly heated in a tube, or slightly, when heated in the air, with red flame and black smoke, leaving a residue of charcoal. — 2. When heated with bromine, it is converted into binitrobromocarbolic acid. (*Rev. scient.* 6, 65.) Chlorine appears not to act upon it. — 3. By boiling nitric acid it is quickly converted into picric acid. (Laurent.) — 4. When heated with chlorate of potash and hydrochloric acid, it is very easily converted into chloranil. (Hofman, *Ann. Pharm.* 52, 62.) — 5. It dissolves in warm fuming oil of vitriol, and then decomposes, with rapid evolution of gas, turning brown and thickening at the same time. — 6. It dissolves gradually in dilute sulphuric acid, in presence of zinc, forming a rose-coloured liquid, which is turned green by excess of ammonia, without precipitation. — 7. When digested with aqueous oil of vitriol and baryta, out of contact of air, it forms a blood-red liquid. (Laurent.) — 8. When gently heated with aqueous hydrosulphate of ammonia, it forms a nearly black liquid, which, on cooling, deposits black-brown needles of nitrodifunamic acid, $C^{24}Ad^2X^2H^8, O^4 + 4\,Aq$; thus:

$$2C^{12}N^2H^4O^{10} + 12HS = C^{24}N^4H^{16}O^{16} + 4HO + 12S.$$

(Laurent and Gerhardt, *Ann. Pharm.* 75, 68.)

*Combinations.* The acid is nearly insoluble in cold water, and dissolves but sparingly in boiling *water.*

It dissolves abundantly in warm *oil of vitriol,* whence it is precipitated by water.

It dissolves slightly in boiling *hydrochloric acid,* and separates in fern-like tufts on cooling.

The *Binitrocarbolates* or *Nitrophenesates* are obtained, sometimes by saturating the acid with the pure base or its carbonate, sometimes by double decomposition. They are yellow or aurora-red and crystallisable. They all dissolve in water, and in this form impart a strong yellow colour to animal tissues. Heated somewhat above the melting point of lead, they detonate very slightly, with emission of light. Sulphuric, hydrochloric and nitric acid separate the acid from them.

*Binitrocarbolate of Ammonia.* — Crystallises from boiling water in long thin yellow needles having a silky lustre. By sublimation, yellow shining laminæ are obtained. *Fig.* 68, without $p$ and $e$; $u : t = 144° 30'$. (*Rev. scient.* 9, 26.) Very sparingly soluble in water, still less in alcohol. (Laurent.)

*Binitrocarbolate of Potash.* —Yellow, shining, six-sided needles, with angles of 115°. They redden whenever they are heated, without alteration of weight; decompose and become opaque below 100°; give off 3·90 p. c. water in vacuo at 100°; melt at a stronger heat, and then detonate. They dissolve sparingly in cold water, very sparingly in cold alcohol, more easily in hot alcohol. (Laurent.)

| | | | Laurent. |
|---|---|---|---|
| $C^{12}N^2H^3O^9$ | 175·0 | 75·69 | |
| KO | 47·2 | 20·42 | 20·14 |
| HO | 9·0 | 3·89 | 3·90 |
| $C^{12}X^2H^3KO^2 + Aq$ | 231·2 | 100·00 | |

*Binitrocarbolate of Soda.* — Yellow, silky needles, which dissolve pretty easily in water. (Laurent.)

*Binitrocarbolate of Baryta.* — Aurora-red (like bichromate of potash), thick, six-sided oblique prisms and needles, with two angles of the lateral edges of 89°, and four of 135° 30′. In vacuo, at ordinary temperatures, they give off 6·5 p. c. (2 At.) and at 100° altogether, 15·42 p. c. (5 At.) water.

| | *Crystals.* | | Laurent. |
|---|---|---|---|
| $C^{12}N^2H^3O^9$ | 175·0 | 59·00 | |
| BaO | 76·6 | 25·83 | 25·62 |
| 5 HO | 45·0 | 15·17 | 15·42 |
| $C^{12}X^2H^3BaO^2 + 5Aq$ | 296·6 | 100·00 | |

The ammonia-salt, mixed with *chloride of strontium*, the solutions being hot and concentrated, soon forms silky needles; with *chloride of calcium*, granules consisting of needles; with *alum*, needles. It does not precipitate salts of *magnesium, manganese, cadmium, cobalt, nickel*, or *copper*, or *mercuric salts.*

*Binitrocarbolate of Lead.* — *a. Bibasic.* — The yellow precipitate which the ammonia-salt produces in a boiling dilute solution of neutral acetate of lead. It detonates with peculiar violence when heated, and gives off 8·4 p. c. water in vacuo at ordinary temperatures, 9·4 p. c. in all at 100°.

*b. Sesquibasic.*—The boiling, moderately concentrated mixture of alcoholic binitrocarbolic acid and alcoholic acetate of lead, yields on cooling, microscopic needles grouped in yellow balls, which do not give off any water at 150°. (Laurent.)

| Salt *a*. | | | Laurent. |
|---|---|---|---|
| $C^{12}N^2H^3O^9$ | 175 | 40·23 | |
| 2 PbO | 224 | 51·49 | 50·6 |
| 4 HO | 36 | 8·28 | 9·4 |
| $PbO,C^{12}X^2H^3PbO^2 + 4Aq$ | 435 | 100·00 | |

| Salt *b*. | | | Laurent. |
|---|---|---|---|
| 2 $C^{12}N^2H^3O^9$ | 350 | 51·02 | |
| 3 PbO | 336 | 48·98 | 49 |
| $PbO,2C^{12}X^2H^3PbO^2$ | 686 | 100·00 | |

*Binitrocarbolate of Cobalt.*— Brown-yellow, right rectangular prisms, with dihedral summits. Its brown aqueous solution forms with ammonia a yellow precipitate which melts and detonates when heated. (Laurent.)

*Binitrocarbolate of Copper.* — Yellow silky needles, whose yellow solution forms with ammonia, yellow needles sparingly soluble in ammonia or in water. (Laurent.)

*Binitrocarbolate of Silver.* — The ammonia-salt forms with solution of nitrate of silver, a reddish yellow precipitate, or in case of greater dilution, after a while, needles which dissolve in a large quantity of water or alcohol. (Laurent.)

Binitrocarbolic acid dissolves very readily in *alcohol* and in *ether*. (Laurent.)

### *Nitrobromine-nucleus* $C^{12}X^2BrH^3$.

## Binitrobromocarbolic Acid.

$C^{12}N^2BrH^3O^{10} = C^{12}X^2BrH^3,O^2$.

LAURENT. *Rev. scient.* 6, 65.

*Binitrobromocarbolsäure, Acide nitrobromophénisique.*

*Preparation.* Binitrocarbolic acid is dissolved in heated bromine; the crystals which separate on cooling, washed with a small quantity of alcohol, and dissolved in boiling ether; and the solution left to crystallise in a beaker-glass covered with paper.

*Properties.* Sulphur-yellow, transparent. Crystallises from ether in shining oblique rhombic prisms. *Fig.* 81, the corners between $u$, $u'$ and $i$, being replaced by two faces, which form with $u$ or $u'$ an angle of about 152°; $u' : u'' = 106° 30'$; $i : u$ or $u' = 98° 30'$. — From boiling water or alcohol, it separates in needles. Melts at about 110°, and solidifies on cooling into a laminar fibrous mass. When strongly heated, it distils partly undecomposed and leaves a small quantity of charcoal. Permanent in the air, inodorous, colours the skin yellow, like picric acid.

| *Crystals.* | | | Laurent. |
|---|---|---|---|
| 12 C | 72 | 27·37 | 27·49 |
| 2 N | 28 | 10·65 | 11·20 |
| Br | 80 | 30·42 | 29·50 |
| 3 H | 3 | 1·14 | 1·20 |
| 10 O | 80 | 30·42 | 30·61 |
| $C^{12}N^2BrH^3O^{10}$ | 263 | 100·00 | 100·00 |

*Decompositions.* 1. The acid is not decomposed by chlorine in the cold and but slightly when heated. — 2. By boiling nitric acid it is converted into picric acid. — 3. Its solution in warm oil of vitriol decomposes when heated. — 4. Its aqueous solution forms with ferrous sulphate and lime, a blood-red liquid, with precipitation of ferric oxide.

*Combinations.* The acid dissolves very sparingly in boiling *water* and separates almost completely on cooling.

It dissolves in warm *oil of vitriol,* whence it crystallises in fern-like groups.

The *Binitrobromocarbolates* or *Nitrobromophenisates* are yellow, orange-coloured or red; crystallise well; resemble the picrates; detonate for the most part, like those salts, when heated, but less strongly, and in a closed space, with emission of light; and dissolve for the most part in water, from which solution, sulphuric, hydrochloric, or nitric acid separates the binitrobromocarbolic acid.

*Binitrobromocarbolate of Ammonia.* — Yellow eight-sided needles derived from a rhombic prism. In vacuo at 100° they give off 8·57 p. c. water, and 1·86 p. c. more at a heat nearly sufficient to volatilise them, and then sublime, for the most part undecomposed, in yellow, shining right rhombic prisms, with lateral edges of 45° and 135°.

The *potash-salt* forms yellow, silky needles, sparingly soluble in water and alcohol.

*Baryta-salt.* — The dark yellow needles, which dissolve very readily in water, give off in vacuo at ordinary temperatures, 7·5 p. c. (3 At.) water, assuming a scarlet colour, and at 100°, 9·42 p.c. (4 At.) in all.

| *Crystals.* | | | Laurent. |
|---|---|---|---|
| $C^{12}N^2H^2O^9$ | 174·0 | 47·47 | |
| Br | 80·0 | 21·82 | 21·8 |
| BaO | 76·6 | 20·89 | 20·5 |
| 4 HO | 36·0 | 9·82 | 9·42 |
| $C^{12}N^2BrH^2BaO^{10} + 4Aq$ | 366·6 | 100·00 | |

*Lime-salt.* — Long yellow laminæ, which are oblique rectangular prisms. They turn about on recently dried paper or in vacuo, giving off water and assuming a scarlet colour.

The ammonia-salt does not form any precipitate with chloride of strontium, magnesium or manganese.

*Lead-salt.* — When a boiling dilute solution of the ammonia-salt is poured into a boiling dilute solution of neutral acetate of lead, there is immediately formed an orange-yellow precipitate of the $\frac{4}{3}$-basic salt containing 37 p. c. lead-oxide; and the liquid decanted therefrom after

some seconds, forms pale yellow silky needles of the bibasic salt, which give off 3·3 p. c. (2 At.) water in vacuo at 100°, and contain 44·0 p. c. lead-oxide. — In solutions not too dilute, the ammonia-salt forms with lead-salts, a heavy, yellow, crystalline precipitate.

The ammonia-salt forms with the salts of *cadmium*, *cobalt*, *nickel* and *copper*, on addition of ammonia, a precipitate which consists of needle-shaped particles, scarcely soluble in ammonia.

With *nitrate of silver*, the ammonia-salt forms a yellow translucent precipitate, and in case of great dilution, it gradually forms tenacious threads.

The acid dissolves pretty easily in boiling alcohol, separating out on cooling, and more easily in ether. (Laurent.)

## *Nitrochlorine-nucleus* $C^{12}XCl^2H^3$.

## Nitrobichlorocarbolic Acid.

$$C^{12}NCl^2H^3O^6 = C^{12}XCl^2H^3,O^2.$$

LAURENT & DELBOS. (1845.) *N. Ann. Chim. Phys.* 19, 380; also *J. pr. Chem.* 40, 382; abstr. *Compt. rend.* 21, 1419.

*Nitrobichlorocarbolsäure, Acide phénique nitrobichloré.*

Chlorine gas is passed through that portion of coal-tar oil which boils between 180° and 200°; a small quantity of water added; the liquid neutralised with ammonia, boiled with water, and filtered from the brown matter; the filtrate neutralised with nitric acid; and the crystals of nitrobichlorocarbolic acid which separate on cooling, purified by repeated recrystallisation from alcohol.

*Properties.* Yellow oblique rhombic prisms. The acute lateral edges = 88°; angle between the base and a lateral face = 108° 20′ to 30′.

| | *Crystals.* | | Laurent & Delbos. |
|---|---|---|---|
| 12 C | 72·0 | 34·65 | 34·70 |
| N | 14·0 | 6·74 | |
| 2 Cl | 70·8 | 34·07 | 33·00 |
| 3 H | 3·0 | 1·44 | 1·55 |
| 6 O | 48·0 | 23·10 | |
| $C^{12}NCl^2H^3O^6$ | 207·8 | 100·00 | |

The acid, when suddenly heated in a close vessel, decomposes with fire.

Easily soluble in *water*.

*Ammonia-salt.* — Aurora-red needles, which, when carefully heated, sublime partly undecomposed. Contains 31·2 p. c. chlorine, and is therefore $C^{12}XCl^2H^2(NH^4)O^2$.

*Potash-salt.* — Shining laminæ, carmine-coloured or yellow by reflected light, according to the angle at which they are viewed. Contains 18·5 p. c. potash, therefore probably = $C^{12}XCl^2KO^2$.

The other salts likewise resemble the picrates.

The acid dissolves with tolerable facility in *alcohol* and *ether*, and crystallises out on cooling. (Laurent and Delbos.)

## Binitrochlorobenzene.

$C^{12}N^2ClH^3O^8 = C^{12}X^2ClH^3$.

LAURENT & GERHARDT. *Compt. chim.* 1849, 429; abstr. *Ann. Pharm.* 75, 79.

*Binitrochlorophénile, Binitrochlorfune.*

When binitrocarbolic acid is decomposed by pentachloride of phosphorus, there is formed, with evolution of hydrochloric acid and oxychloride of phosphorus, a solution of excess of pentachloride of phosphorus in binitrochlorobenzene, which, when cold, may be decanted from the chloride of phosphorus which has crystallised out. — The compound is perhaps formed in this manner :

$$C^{12}X^2H^4O^2 + PCl^5 = C^{12}X^2ClH^3 + PCl^3O^2 + HCl.$$

The yellowish oil which sinks to the bottom without dissolving, solidifies in a few days in the crystalline form, and is washed with cold alcohol, which dissolves a small portion of it. The solution of the crystals in hot alcohol becomes milky on cooling, and deposits a yellowish oil, which after a few hours solidifies in needles. (Laurent and Gerhardt.)

*Nitro-nucleus* $C^{12}X^3H^3$.

## Ternitrocarbolic or Picric Acid.

$C^{12}N^3H^3O^{14} = C^{12}X^3H^3,O^2$.

HAUSMANN. *J. Phys.* 1788, März.
WELTER. *Ann. Chim.* 29, 301 ; also *Scher. J.* 3, 715.
FOURCROY & VAUQUELIN. *N. Gehl.* 2,231.
CHEVREUL. *Ann. Chim.* 72, 113; also *Gilb.* 44, 150.
MORETTI. *Brugn. Giorn.* 17, 415; also *Schw.* 51, 69.
LIEBIG. *Schw.* 49, 373, 51, 374. — *Pogg.* 13, 191. — *Kastn. Arch.* 13, 353; also *Ann. Chim. Phys.* 37, 286. — *Ann. Pharm.* 9, 82. — *Pogg.* 14, 466.
WÖHLER. *Pogg.* 13, 488.
DUMAS. *Ann Chim. Phys.* 53, 178; also *Pogg.* 29, 98; also *Ann. Pharm.* 9, 80. — *N. Ann. Chim. Phys.* 2, 228; also *Ann. Pharm.* 39, 350 ; also *J. pr. Chem.* 24, 215.
E. SCHUNCK. *Ann. Pharm.* 39, 7; 65, 234.
LAURENT. *N. Ann. Chim. Phys.* 3, 221; also *Ann. Pharm.* 43, 219; also *J. pr. Chem.* 25, 424.
R. F. MARCHAND. *J. pr. Chem.* 23, 363; 26, 397; 32, 35; 44, 91.

STENHOUSE. *Phil. Mag. J.* [3] 28, 440; also *Ann. Pharm.* 57, 84; also *J. pr. Chem.* 39, 221 — Further: *Phil. Mag. J.* [4], 8, 36; *Ann. Pharm.* 91, 307; *J. pr. Chem.* 62, 464; *Pharm. Centr.* 1854, 619; *Jahresber.* 1854, 466.

*Artificial Indigo-bitter, Chevreul's artificial Bitter with maximum of Nitric acid, Welter's Bitter, Carbazotic acid, Kohlenstickstäure, Kohlenstickstoffsäure* v. Liebig, *Nitropicric acid, Pikrinsalpetersäure, Nitrophenisic acid, Chrysolepic acid* (from aloes), *Jaune amer de Welter, Jaune amer, Acide carbo-azotique, Acide pikrique* of Dumas, *Ac. nitrophenisique* of Laurent. — Discovered by Hausmann in 1788; examined with regard to its composition, by Liebig, Dumas & Laurent.

*Formation.* 1. By the action of heated nitric acid on carbolic, terbromocarbolic and binitrocarbolic acid (Laurent), on saligenin, salicylous acid, salicin (Piria), salicylic acid, nitrosalicylic acid, phlorizin (Marchand), extract of willow-bark (Böttger & Will), indigo (Hausmann), cumarin (Delalande), aloes (Schunck), benzoin (E. Kopp), resin from Botany Bay, resin of Peru balsam (Stenhouse), and silk. (Welter.) Myrrh, quinine, morphine, and narcotine do not yield the acid (Liebig); whether it is contained in the yellow bitter substance into which albumin, fibrin, the crystalline lens, casein, and gluten, are converted by nitric acid, remains to be determined. — 2. By boiling ternitranisol ($C^{12}X^3H^5O^2$) with potash-ley. (Cahours.)

*Preparation.* I. *From Carbolic acid.* The brown resinous masses precipitated during the preparation of binitrocarbolic acid (p. 206), are united with the mass obtained by precipitating with nitric acid the mother-liquors of binitrocarbolate of ammonia obtained in the same process; the united mass heated to the boiling point in a basin with commercial nitric acid; the acid liquid decanted after cooling; the residue washed with a small quantity of cold water, and boiled with very dilute ammonia; the filtrate repeatedly evaporated to the crystallising point; the resulting picrate of ammonia purified by crystallisation from boiling alcohol; and the beautiful needles of this salt treated with nitric acid to separate the picric acid, the quantity of which, thus obtained, is greater as the quantity of binitrocarbolic acid was less. The impure binitrocarbolic acid may also be converted into picric acid by boiling it with nitric acid, and recrystallising from alcohol the portion which separates out. (Laurent.)

II. *From Salicin.* This substance treated with nitric acid yields remarkably pure picric acid, whereas phlorizin yields much less picric than phloretic acid. (Marchand.)

III. *From Indigo.* 12 to 13 pts. of nitric acid of sp. gr. 1·43 are heated nearly to the boiling point in a capacious glass flask; 1 pt. of the best East Indian indigo in coarse powder, added in small portions, each addition being made as soon as the last portion has disappeared; the red-brown liquid concentrated by boiling till it becomes thickish and lighter in colour; 3 pts. more nitric acid added in case the liquid still gives off nitrous acid, and the boiling repeated: the mother-liquor decanted from the hard yellow, translucent crystals which form on cooling; these crystals washed with cold water and dissolved in a sufficient quantity of boiling water; the oily drops of artificial tannin which then rise to the surface removed with filtering paper; the solution filtered and left to cool; the yellow shining laminæ of picric acid which separate removed

from the mother-liquor, again dissolved in boiling water, and neutralised with carbonate of potash; and the potash-salt which separates on cooling purified by repeated crystallisation, then dissolved in boiling water, and the liquid mixed with sulphuric, hydrochloric or nitric acid, whereupon the picric acid crystallises out on cooling. A large quantity of the potash-salt, requiring however further purification, may also be obtained from the first mother-liquor by precipitating therefrom a large quantity of brown matter by addition of water, then dissolving it in boiling water, neutralising with carbonate of potash, and cooling.— 4 pts. of indigo yield 1 pt. of picric acid. — Sometimes the solution of indigo in nitric acid does not yield any crystals; it must then be evaporated down, mixed with water, and the acid separated from the brown precipitate as above. The liquid above the precipitate likewise yields picric acid, when evaporated, boiled with nitric acid, neutralised with potash, &c. (Liebig.) — Moretti used 14 pts. of nitric acid of sp. gr. 1·30 to 1 pt. of indigo, whereas Chevreul used only 2 pts. nitric acid, and therefore obtained chiefly nitrosalicylic (indigotic) acid, artificial indigo-resin, &c., mixed with only a small quantity of picric acid. If the indigo be boiled with 12 pts. of nitric acid, not merely for a few, but for 30 hours, till in fact only traces of the indigo-resin at first produced, remain, red vapours are continually evolved and the greater part of the picric acid is destroyed, so that ultimately the product amounts to only $\frac{1}{64}$ of the indigo. (Blumenau, *Ann. Pharm.* 67, 115.)

IV. *From the Yellow Resin of Botany Bay.*—The resin of *Xanthorrhœa hastilis* is dissolved in the requisite quantity of strong nitric acid, whereupon red vapours are evolved, with violent frothing, and a dark-red solution formed which becomes deep yellow after boiling. This solution is evaporated over the water-bath; the remaining yellow crystalline mass, which, together with picric acid, contains small quantities of oxalic and nitrobenzoic acid, neutralised with potash; the picrate of potash purified by two crystallisations, and then treated with hydrochloric acid, which separates the picric acid, to be further purified by two crystallisations, and amounting to 50 per cent. of the resin used. (Stenhouse.)

V. *From Benzoin.* 1 pt. of benzoin (from which the benzoic acid may be previously extracted by alkalis: *Kopp, Stenhouse*), is gently heated with 8 pts. of commercial nitric acid; the mixture distilled, with four times repeated cohobation, after the effervescence has ceased; and the liquid, after decantation from the resin, mixed with four times its bulk of water, filtered from the precipitated yellow powder, and neutralised while hot with carbonate of potash: it then yields crystals of picrate of potash on cooling. (E. Kopp, *N. Ann. Chim. Phys.* 13, 233.)

VI. *From Silk.* — 1. When 1 part of silk is distilled, with frequent cohobation, with 6 pts. of nitric acid, a solution is obtained which, by evaporation and cooling, yields crystals of picric and oxalic acid. (Welter.) — 2. In this process, 12 pts. of nitric acid are used; the residue in the retort is neutralised with carbonate of potash; the crystals of picrate of potash purified by recrystallisation; and the acid precipitated from their solution by nitric acid. The product from silk is however much smaller than that which is obtained from indigo. (Liebig.)

VII. *From Aloes.* 1. pt. of aloes is heated with 8 pts. of strong nitric acid till violent action takes place; the fire then removed; the mixture, after the gas-evolution has ceased, introduced into a retort; the greater part of the acid liquid poured off; the residue distilled with 3 or 4 pts. of fresh nitric acid, which still causes a slow evolution of

nitric oxide, till the greater part of the nitric acid is decomposed or volatilised; the residue diluted with water, which separates the chrysammic and aloetic acids still remaining undecomposed; the yellow filtrate evaporated, in order to remove the greater part of the nitric acid; then neutralised with milk of lime; and pure picric acid precipitated from the filtrate by nitric acid.— Schunck formerly left the evaporated liquid to crystallise; purified the crystals of picric acid from those of oxalic acid by careful washing with cold water; combined the remaining acid with potash; purified the salt by crystallisation, &c.; and thereby obtained his *Chrysolepic acid*, which he regarded as isomeric, but not identical with picric acid. But the experiments of E. Robiquet, (*N. J. Pharm.* 13, 44; 14, 179), of R. F. Marchand, (*J. pr. Chem.* 44, 91), of Mulder (*J. pr. Chem.* 48, 1), and of Schunck himself (*Ann. Pharm.* 65, 234) soon led to the conclusion that the supposed peculiar characteristics of chrysolepic acid were due to small quantities of admixed chrysammic or aloetic acid.

VIII. *From Ternitranisol.* Ternitranisol is boiled for a few minutes with moderately strong potash; water added till all the resulting potash-salt is dissolved; the salt allowed to crystallise by cooling; and the acid separated therefrom by boiling dilute nitric acid: it then separates on cooling in yellow shining needles, and may be purified by washing with cold water and crystallisation from boiling water. (Cahours, *N. Ann. Chim. Phys.* 25, 26; also *J. pr. Chem.* 46, 337).

[Cahours regards this acid, called *Picranisic acid*, as isomeric but not identical with picric acid, inasmuch as it exhibits differences in the crystalline form and fusibility, as also in its appearance and in the solubility of some of its salts. Till however these peculiarities are more clearly made out, and shown to be not merely accidental, the acid may be regarded as picric acid. All statements respecting picric acid cited from Cahours relate to this *picranisic acid*, and those of Schunck to the *acid obtained from aloes.*]

*Properties.* Light yellow, strongly shining laminæ. (Liebig.) Yellowish octohedrons, often very much truncated on two of their summits (Welter); yellowish white needles and granules (Chevreul.) Crystalline system, the right prismatic; *Fig.* 66 without the faces $y$ and $m$ and those between $t$ and $a$; $a : u' = 128° 36'$; $u : t = 115° 42'$ ($115° 30'$, according to Laurent); $a : a = 109° 50'$ ($108°$; $t : a = 125°$: Laurent, *Rev. scient.* 9, 24); $a : u = 125° 5'$, $a : a$ behind $= 111° 57'$ (Mitscherlich, *Pogg.* 13, 375). — The acid from indigo crystallises from hot water in lemon-yellow, opaque laminæ, which become yellowish brown and transparent in warm air, crystallise from alcohol in transparent yellowish brown laminæ, and from ether in transparent yellowish brown prisms, which become lemon-yellow and dull on exposure to the air, but recover their original appearance when strongly breathed upon. (Blumenau.)— *Chrysolepic acid;* golden-yellow shining scales. (Schunck.) — *Picranisic acid*: small hard, highly lustrous prisms. (Cahours.) — The acid melts (Liebig) when slowly heated, forming a brownish yellow oil, which solidifies in a crystalline mass on cooling. (Schunck.) When slightly heated in contact with the air, it volatilises undecomposed (Liebig, Welter); at a higher temperature, it boils and gives off a thick, yellow, suffocating, irritating, and intensely bitter vapour (Schunck), and sublimes in small yellowish white needles and scales (Fourcroy & Vauquelin, Chevreul), or passes over as a brown liquid which crystallises on cooling. (Schunck.) — It tastes very bitter and somewhat harsh and sour, and reddens litmus. (Fourcroy & Vauquelin, Chevreul, Liebig.) The impure acid from indigo in doses of 1 to 10 grains, kills rabbits and dogs with delirium and convulsions. (Rapp, *Rapp et Föhr, Diss. de effectib. venen. mat. am. Waltheri;* Tub. 1821.)

| | | | | Laurent, *from carbolic acid.* | | Marchand, *from salicin.* | | *from salicylic acid.* |
|---|---|---|---|---|---|---|---|---|
| 12 C | 72 | .... | 31·44 | 31·82 | ........ | 31·34 | ........ | 31·38 |
| 3 N | 42 | .... | 18·34 | 18·62 | ........ | 18·51 | ........ | 18·60 |
| 3 H | 3 | .... | 1·31 | 1·41 | ........ | 1·57 | ........ | 1·54 |
| 14 O | 112 | .... | 48·91 | 48·15 | ........ | 48·58 | ........ | 48·48 |
| $C^{12}N^3H^3O^{14}$. | 229 | .... | 100·00 | 100·00 | ........ | 100·00 | ........ | 100·00 |

| | Liebig, *from Indigo,* *earlier.* | | *later.* | Dumas, *from Indigo,* *earlier.* | | *later.* | Erdmann & Marchand, *from Indigo.* |
|---|---|---|---|---|---|---|---|
| C | 31·92 | .... | 35·04 | 31·8 | .... | 31·88 | 31·45 |
| N | 14·99 | .... | 16·18 | 18·5 | .... | 18·50 | 18·49 |
| H | | .... | | 1·4 | .... | 1·45 | 1·37 |
| O | 53·09 | .... | 48·78 | 48·3 | .... | 48·17 | 48·69 |
| | 100·00 | .... | 100·00 | 100·0 | .... | 100·00 | 100·00 |

| | Stenhouse, *from resin of Botany Bay.* | Schunck, *from Aloes.* | Mulder, *from Aloes.* | Cahours, *from Ternitranisol.* |
|---|---|---|---|---|
| C | 31·53 | 32·12 | 31·4 | 31·29 |
| N | | 18·60 | 18·0 | 18·40 |
| H | 1·42 | 1·41 | 1·4 | 1·31 |
| O | | 47·87 | 49·2 | 49·00 |
| | | 100·00 | 100·0 | 100·00 |

Liebig always found a certain quantity of H, which he formerly regarded as unessential, but (*Ann. Pharm.* 9, 82), estimated at 1·10 p. c.

The crystallised acid mixed with 5 times its weight of lead-oxide and with water, and dried, ultimately in vacuo at 100°, gives off 3·6 p. c. water (1 At. amounts to 3·93 p. c. Laurent), 1 At. water is also set free when the acid combines with potash, soda, or oxide of silver. (Marchand.)

*Decompositions.* 1. The acid, when quickly *heated* in a retort, melts (boils violently, according to Shunck) and blackens with explosion, and then takes fire, giving off nitrogen, nitric oxide, nitrous acid, water, carbonic acid, hydrocyanic and a combustible gas (depositing a large quantity of soot, according to Schunck), and leaves charcoal. (Chevreul.)—2. When quickly heated in contact with the air, both the melting acid and its vapour take fire and burn with a yellow, very smoky flame (Liebig), and leave a small quantity of charcoal. (Schunck.)

3. When chlorine gas is passed for several days through the aqueous acid, or when the acid is distilled with aqueous chloride of lime, which then becomes heated and deposits carbonate of lime,—or with chlorate of potash and hydrochloric acid, the picric acid is resolved into chloropicrin which distils over, and chloranil, the greater part of which remains behind. Boiling aqua-regia acts in a similar manner, excepting that it produces more chloropicrin and less chloranil. (Stenhouse, *Phil. Mag. J.* 33, 53; also *Ann. Pharm.*, 66, 241; Hofmann, *Ann. Pharm.* 52, 62.)—In a similar manner, picric acid is resolved, by heating with bromine and water, into bromopicrin and bromanil. (p. 217.) — It is also converted

into bromopicrin by distillation with hypobromite of lime. (Stenhouse, *Phil. Mag. J.* [4], 8, 36.) Chlorine gas does not decompose the acid (not even in the melted state; *Schunck*), neither does melted iodine (or bromine: *Marchand*), or chlorine water, chloride of gold, or hydrochloric acid, even at the boiling heat; even boiling aqua-regia scarcely acts upon it. (Liebig.) But nitric acid boiled with it for several days, appears under certain circumstances to exert a decomposing action. (Blumenau.)

We may here insert, as an appendix, the description of chloropicrin and bromopicrin, which have been discovered since the publication of the portion of this Handbook relating to the 2-carbon compounds.

## Chloropicrin. $C^2NCl^3O^4 = C^2XCl^3$.

STENHOUSE. (1848.) *Phil. Mag. J.* [3], 33, 53; also *Ann. Pharm.* 66, 241; also *J. pr. Chem.* 45, 56.— Gerhardt and Cahours. *Compt. Chim.* 1849, 34 and 170.

*Formation.* 1. By the distillation of picric acid, styphnic acid or chrysammic acid with chloride of lime and water. Hence also when the bodies which yield either of these three acids by treatment with nitric acid, are first boiled with nitric acid and then distilled with chloride of lime. To these belong: Creosote, salicin, indigo, cumarin, the yellow resin of Botany Bay, liquid storax, benzoin, Peru-balsam, galbanum, gum asafœtida, gum-ammoniacum, purree, aloes, extract of Campeachy wood, log-wood, fustic, red sandal-wood, &c. Lastly, Dammara resin, and the chlorinated resin formed in the decomposition of usnic acid by chlorine, likewise yield chloropicrin when treated with nitric acid and chloride of lime. — 2. By treating picric acid with chlorine-water or aqua-regia, or a mixture of chlorate of potash and hydrochloric acid. (Stenhouse.)

*Preparation.* Aqueous picric acid is distilled with chloride of lime, till, after about a quarter of an hour's boiling, no more heavy oil passes over with the water. Should the residue be still yellow, it must be redistilled with fresh chloride of lime. The oil is separated from the watery distillate, washed with water to which a little carbonate of magnesia has been added, dried by placing it over chloride of calcium, and rectified. (Stenhouse.)

*Properties.* Transparent, colourless oil, of sp. gr. 1·6657; refracts light strongly; boils at 120°. Its odour, in the dilute state, is peculiarly aromatic, but in the concentrated state very sharp, and attacks the nose and eyes, less persistently, but quite as violently, as volatile chloride of cyanogen and oil of mustard. It is neutral to vegetable colours. (Stenhouse.)

Calculation, according to Gerhardt.

| | | |
|---|---|---|
| 2 C | 12·0 | 7·31 |
| N | 14·0 | 8·52 |
| 3 Cl | 106·2 | 64·68 |
| 4 O | 32·0 | 19·49 |
| $C^2XCl^3$ | 164·2 | 100·00 |

| Calculation according to Stenhouse. | | | Stenhouse. | Cahours. |
|---|---|---|---|---|
| 4 C | 24·0 | 6·32 | 6·58 | 7·14 |
| 2 N | 28·0 | 7·37 | 7·68 | |
| 7 Cl | 247·8 | 65·25 | 61·79 | 61·43 |
| 10 O | 80·0 | 21·06 | 20·73 | |
| | | | H 0·22 | |
| | 379·8 | 100·00 | 100·00 | |

*Decompositions.* 1. Chloropicrin sustains, without alteration, a heat of 150°; but when passed through a red-hot tube, it is completely decomposed, yielding nitric oxide, chlorine, and sesquichloride of carbon. — 2. It is not decomposed, even by prolonged contact with aqueous potash, but gradually by alcoholic potash, with separation of chloride of potassium and nitrate of potash. — 3. Aqueous ammonia exerts scarcely any action upon chloropicrin; but ammoniacal gas or alcoholic ammonia produces sal-ammoniac and nitrate of ammonia. — 4. A small piece of potassium gently heated in the oil, causes strong explosion; at ordinary temperatures, it produces in a few days chloride of potassium and nitre. — Sulphuric, nitric, and hydrochloric acid do not act upon it, even at a boiling heat. (Stenhouse.)

*Combinations.* Chloropicrin dissolves very sparingly in water, but with great facility in alcohol and ether. — (Stenhouse.)

## ¶. Bromopicrin. $C^2NBr^3O^4 = C^2XBr^3$.

STENHOUSE. *Phil. Mag. J.* [4], 8, 36; *Ann. Pharm*, 91, 307; *J. pr. Chem.* 62, 464; *Pharm. Centr.* 1854, 619; *Jahresber*, 1854, 466.

*Formation.* (*p.* 216.)

*Preparation.* — 1. Picric acid is distilled with a solution of hypobromite of lime, and the product washed with aqueous carbonate of soda, shaken up with mercury to remove free bromine, and dehydrated by digestion (not distillation) with chloride of calcium, which does not dissolve in it. — 2. When picric acid is digested for some hours with bromine and water, bromopicrin is obtained of a yellow colour arising from the presence of free bromine, which may be removed as above; but the product is still impure, probably containing a bromide of carbon $C^2Br^4$, produced by the continued action of bromine on the bromopicrin.

*Properties.* — Prepared by (1): Colourless liquid, heavier than water, and smelling very much like chloropicrin; its vapour attacks the eyes very strongly. Boiling point above 100°.

| | | | Stenhouse. (1.) | Stenhouse. (2.) |
|---|---|---|---|---|
| 2 C | 12 | 4·03 | | |
| N | 14 | 4·66 | | |
| 3 Br | 240 | 80·54 | 80·015 | 85·3 |
| 4 O | 32 | 10·77 | | |
| $C^2XBr^3$ | 298 | 100·00 | | |

The excess in the analysis (2) is probably due to the presence of $C^2Br^3$. (*vid. sup.*)

Bromopicrin may be heated nearly to its boiling point without alteration; but when it begins to boil, it is decomposed, with evolution of

brown-red vapours, even in an atmosphere of carbonic acid. At a higher temperature, it is decomposed, with slight explosion.

Dissolves very sparingly in *water*, but readily in *alcohol* and *ether*. The alcoholic solution is not immediately precipitated by nitrate of silver, but after some time, in the cold, and immediately on the application of heat, bromide of silver is precipitated. (Stenhouse.) ¶.

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4. Picric acid gently heated with *peroxide* of manganese and sulphuric acid, becomes hot and gives off nitrous vapours. (Wöhler.)

5. Picric acid boiled with strong potash-ley in excess is decomposed (according to Dumas, *Ann. Chim. Phys.* 53, 186, with abundant evolution of ammonia), and an opaque brown solution formed, from which boiling alcohol extracts a yellow needle-shaped salt, which decolorises tincture of indigo when boiled with it in presence of sulphuric acid. (Wöhler.)—When picric acid is mixed with excess of baryta-water and the liquid boiled down to dryness, the residual mass, which is at first yellowish red, becomes brownish yellow; gives off when boiled down with fresh water, a large quantity of ammonia; and the residue, if then exhausted by boiling with water (while the mass on the filter contains no more picric acid, but evolves a large quantity of prussic acid when treated with hydrochloric acid) yields a pale yellow filtrate, which is free from picric acid, but contains free baryta, cyanide of barium, and a yellowish amorphous salt which gives off nitric acid when acted upon by oil of vitriol. (Wöhler.)

6. Picric acid digested, as in the cold indigo-vat, with protosulphate of iron, excess of hydrate of lime or baryta, and water, yields a brown red mass; and the resulting brown red filtrate, when freed by carbonic acid from excess of alkali, and then filtered and evaporated, leaves a black-brown amorphous compound of deoxidised picric acid with lime or baryta, which dissolves readily and with blood-red colour in water, deflagrates like gunpowder when heated, evolving hydrocyanate of ammonia, and leaves, first a tumefied charcoal, then an alkaline carbonate. When the aqueous solution of the barium-compound is precipitated by neutral acetate of lead and a small quantity of ammonia (to ensure complete precipitation), the lead-compound is obtained in the form of a thick, red-brown precipitate, which explodes by heat as strongly as the lime or baryta-salts, and dissolves sparingly in water, forming a deep yellow solution. By suspending the lead-precipitate in water, decomposing it with sulphuretted hydrogen, frequently exhausting the sulphide of lead with boiling water, and evaporating the dark yellow filtrate, *deoxidised picric acid (nitrohæmatic acid)* is obtained in brown crystalline grains. This acid, when subjected to dry distillation, melts, exhibits a kind of detonation, but without fire, gives off a large quantity of hydrocyanate of ammonia, and leaves a shining charcoal which burns away without residue. The acid dissolves with some difficulty in water, forming a yellow solution. With aqueous solutions of the alkalis, it forms bitter, deep blood-red solutions; and paper moistened with the acid and held over ammonia, becomes as red as if it were moistened with ferric sulphocyanide. The solution of the acid leaves on evaporation, a brown mass, with traces of crystals, which explodes when heated, with emission of fire and a large quantity of hydrocyanate of ammonia (evolving ammonia when treated with potash), and from whose concentrated solution hydrochloric acid throws down the deoxidised picric acid in the pulverulent form. This

acid cannot be reconverted into picric acid by the action of nitric acid. (Wöhler.) The bright blood-red colour which picric acid and its salts produce with ferrous sulphate and excess of aqueous alkali, affords a means of detecting traces of it. (E. Kopp, *N. Ann. Chim. Phys.* 13, 285.) — According to E. Pugh (*Ann. Pharm.* 96, 85), picric acid treated with a very large excess of ferrous sulphate, and subsequently with an alkali, yields a colourless filtrate, which, on addition of an acid, assumes a deep blue colour, gradually passing by boiling or by contact with the air, into purple, yellow, and dingy brown. — ¶. When sulphuretted hydrogen is passed to saturation through an alcoholic solution of picric acid saturated in the cold and neutralised with ammonia, the liquid assumes an intense red colour and yields dark red crystals of the ammonia-salt of picramic (or nitrohæmatic) acid, $C^{12}X^2AdH^3O^2$. The formation of this acid is represented by the equation:

$$C^{12}(NO^4)^3H^3O^2 + 6HS = C^{12}(NO^4)^2(NH^2)H^3O^2 + 4HO + 6S.$$

On distilling off the alcohol from the liquid, sulphur is deposited, and an additional crop of crystals of the ammonia-salt obtained. (A. Girard, *Compt. rend.* 36, 421; *Ann. Pharm.* 88, 281.) — The identity of nitrohæmatic with picramic acid was suggested by Gerhardt (*Traité de Chim. org.* 3, 46), and has since been established by E. Pugh (*Ann. Pharm.* 96, 83), and by the further experiments of Girard. (*Compt. rend.* 42, 59.) The formation of picramic acid by the action of protosalts of iron on picric acid, as in Wöhler's process, is expressed by the equation:

$$C^{12}(NO^4)^3H^3O^2 + 12FeO + 2HO = C^{12}(NO^4)^2(NH^2)H^3O^2 + 6Fe^2O^3.$$

Protochloride of iron and protochloride of tin act in the same manner as the protosulphate of iron; a similar product, together with a large quantity of dark brown matter, is also formed by the action of zinc on aqueous picric acid. Cuprous oxide does not appear to exert any reducing action upon picric acid. (Pugh.) Picric acid is also converted into picramic acid by the action of ferrous acetate, the sulphides of the alkali-metals, nascent hydrogen, and cuprous chloride. No reducing agent appears capable of removing more than 1 At. $NO^4$ from picric acid. (Girard.) ¶. — 7. By boiling with sulphite of ammonia, picric acid is decomposed in the same manner as nitronaphthalin. (Piria.) — 8. Picric acid takes fire and burns vividly when slightly heated with phosphorus and potassium. (Wöhler.) It detonates moderately, but with vivid emission of light, when struck in contact with sodium.

Pentachloride of phosphorus acts violently on picric acid, forming *chloropicryl*. $C^{12}X^3H^2Cl$: (Pisani, Compt rend. 39, 852.)

$$C^{12}X^3H^3O^2 + PCl^5 = C^{12}X^3H^2Cl + PCl^3O^2 + HCl.$$

*Combinations.* — Picric acid (also the acid from aloes) dissolves at 5° in 160 pts. of *water*, at 15° in 86, at 20° in 81, at 22·5° in 77, at 26° in 73, and at 77° in 26 pts. (Marchand.) The solution has a brighter yellow colour than the acid itself. (Liebig.) From the cold-saturated solution, an equal measure of oil of vitriol throws down the greater part of the acid, *e.g.* $\frac{7}{8}$ from a solution saturated at 22·5°. (Marchand.)

The acid is insoluble in cold, but dissolves in hot oil of vitriol, and is precipitated in its original state on dilution with water. (Liebig.) — It dissolves abundantly in *nitric acid* (Schunck), and even in the fuming acid at a boiling heat without decomposition. (Cahours.)

The *Picrates, Ternitrocarbolates,* or *Nitrophenisates,* are neutral and crystallisable, have a bitter taste, and mostly a yellow colour. They detonate when heated (at the melting point of lead, and more violently than the binitrocarbolates: *Laurent*), or at least deflagrate, like gunpowder; the detonation is strongest in close vessels, and those salts whose base contains the oxygen in the least intimate state of combination, exhibit the weakest detonation. Picrate of potash or baryta heated to redness with a large quantity of chloride of potassium, yields nitrogen and carbonic acid, but no carbonic oxide. (Liebig.)

*Picrate of Ammonia,* — Eight-sided prisms belonging to the right prismatic system, and with four-sided summits. *Fig.* 66, without $y$-faces and without the faces between $a$ and $t$: $u : u' = 69°$; $u : m = 145° 30'$; $a : a = 135°$; $a$ above : $a$ below $= 115°$. (Laurent, *Rev. scient.* 9, 26.) Small yellow, bitter scales, which scarcely detonate when heated. (Hatchett, *N. Gehl.* 1, 369.) Long narrow laminæ having a light yellow colour and strong lustre. When gently heated in a glass tube, they volatilise completely in inflammable vapours; when suddenly heated, they burn without explosion, and leave a large quantity of charcoal. They dissolve readily in water, with difficulty in alcohol. (Liebig.)—The yellow crystals when gently heated, melt, give off their ammonia, and then yield a sublimate of the acid; when suddenly heated, they deflagrate with a hissing noise. (Marchand.) Aqueous picric acid added to ammoniacal salts, throws down a copious precipitate of picrate of ammonia. (H. Rose, *Pogg.* 49, 186.) — *Chrysolepate of ammonia:* Dark brown needles (Schunck); *Picranisate:* Sometimes orange-yellow, sometimes aurora-red needles. (Cahours.)

| | | | Dumas. | Marchand. | Cahours. | |
|---|---|---|---|---|---|---|
| | | | | | *yellow.* | *red.* |
| 12 C | 72 | 29·27 | 29·3 | 29·47 | 29·30 | 29·35 |
| 4 N | 56 | 22·76 | 23·2 | 22·40 | 22·86 | 22·89 |
| 6 H | 6 | 2·44 | 2·6 | 2·49 | 2·49 | 2·45 |
| 14 O | 112 | 45·53 | 44·9 | 45·64 | 45·35 | 45·31 |
| $C^{12}X^3H^2(NH^4)O^2$ | 246 | 100·00 | 100·0 | 100·00 | 100·00 | 100·00 |

*Picrate of Potash.* — Obtained by neutralising with potash a solution of the acid in hot water, — or, according to Liebig, in the state of greatest purity, by digesting an aqueous solution of chloride of potassium with mercurous picrate, then filtering and cooling. Orange-yellow neutral needles. (Welter, Chevreul.) Yellow, highly lustrous, opaque, four-sided needles, several inches long; when obtained from a dilute solution, they appear by reflected light, sometimes red, sometimes green. (Liebig.) The form of the needles is that of *Fig.* 54 elongated, generally with $t$- and $m$-faces; $u : u' = 70°$; $i : i' = 139°$ nearly. (Laurent; *comp.* Miller. *Pogg.* 36, 478.) — The salt assumes an aurora-red tint every time it is heated, but without altering in weight. (Laurent.) It explodes like gunpowder, diffusing a resinous smoke (Welter); it likewise detonates under the hammer, emitting at the same time a reddish white light. (Fourcroy and Vauquelin.) Heated in a glass tube, it detonates violently, yielding soot and hydrocyanic acid (Chevreul); it melts when heated in a glass tube, and explodes immediately afterwards with a tremendous report, shattering the tube and leaving a small residue of charcoal. (Liebig.) Chlorine deprives the solution of its yellow colour and renders it milky. (Welter.) Hydrochloric or nitric acid, added to a solution of

the salt in warm water, abstracts the potash, so that the picric acid crystallises on cooling (Welter); but on evaporating the mixture, the hydrochloric or nitric acid volatilises, and picrate of potash is left. (Chevreul.) An alcoholic solution of picric acid also throws down picrate of potash after a while from an aqueous solution of nitre. (Liebig.) The salt requires at least 260 pts. of water at 15° to dissolve it (Liebig), but dissolves in 14 pts. of boiling water (Chevreul); the solution saturated while hot, solidifies on cooling into a mass composed of needles. (Liebig.) It is insoluble in alcohol. (Liebig.) — *Chrysolepate of potash:* Needles and laminæ, yellowish brown by transmitted, violet and with metallic lustre by reflected light. (Schunck.) *Picranisate of potash:* Chestnut-brown needles with a golden lustre. (Cahours.)

| | *Crystals.* | | Dumas. | Erdmann & Marchand. | Schunck. |
|---|---|---|---|---|---|
| 12 C | 72·0 | 26·95 | 26·7 | 27·30 | 27·41 |
| 3 N | 42·0 | 15·72 | | 15·70 | 15·87 |
| 2 H | 2·0 | 0·75 | 1·1 | 0·81 | 1·02 |
| KO | 47·2 | 17·66 | 16·9 | 17·25 | 17·56 |
| 13 O | 104·0 | 38·92 | | 38·94 | 38·14 |
| $C^{12}N^3H^2KO^{14}$ | 267·2 | 100·00 | | 100·00 | 100·00 |

Liebig estimated the amount of potash in the crystals at 16·21, Laurent at 17·41, Stenhouse at 17·68, and Cahours at 17·65 p. c.

*Picrate of Soda.* — Slender, yellow, shining needles, which behave like the potash-salt, and dissolve in 10 to 14 pts. of water at 15°. (Liebig.) They contain 12·38 p. c. soda and no water of crystallisation, and detonate with some violence when heated. (Marchand.) — *Picranisate of soda:* golden-yellow needles, much more soluble than the potash-salt. (Cahours.)

*Picrate of Baryta.* — *a. Bibasic.* — 1. When the salt *b* is heated to 350° — 370° for 14 hours, and exhausted with water, the salt *a* remains on the filter in the form of a dark brown powder which explodes with extreme violence at 500° to 600°, and contains 40·7 p. c. baryta. — 2. When the salt *b* is boiled for some time with weak baryta-water, a precipitate is formed consisting of the salt *a* mixed with carbonate of baryta; the greater portion of the salt *b* however remains in the filtrate undecomposed. (Marchand.)

*b. Monobasic.* — Separates from the solution of carbonate of baryta in the aqueous acid in hard, dark yellow, four-sided prisms and broad laminæ. They give off 12·5 p. c. water of crystallisation at 100°. They melt when heated and explode violently, especially if the heat be gradually raised, emitting at the same time a very dazzling yellowish flame. They dissolve readily in water: chloride of potassium added to the solution forms in a few minutes a precipitate of picrate of potash. (Liebig.) The crystals are oblique rectangular prisms, which give off 10·0 p. c. (4 At.) water in vacuo at ordinary temperatures, and the whole, amounting to 15·6 p. c. (6 At.) at 150°. (Laurent.) The prisms give off 10·62 p. c. at 100° to 120°, and 11·16 p. c. altogether at 350°, at which temperature however, a portion of the acid goes off together with the water, and on dissolving the residue in water, a small quantity of the salt *a* remains.

(Marchand.) — *Picranisate of baryta:* Golden yellow needles, having a silky lustre, sparingly soluble, and containing 25·41 p. c. baryta. (Cahours.)

| | Crystals. | | Liebig. | Laurent. | Marchand. |
|---|---|---|---|---|---|
| 12 C | 72·0 | 21·08 | | | 20·99 |
| 3 N | 42·0 | 12·30 | | | |
| 7 H | 7·0 | 2·05 | | | 2·17 |
| BaO | 76·6 | 22·42 | 20·87 | 21·66 | 22·27 |
| 18 O | 144·0 | 42·15 | | | |
| $C^{12}N^3H^2BaO^{14} + 5Aq$ | 341·6 | 100·00 | | | |

*Picrate of Strontia.*— Hard, yellow, shining crystals. They give off 11·29 p. c. (4 At.) water at 150°, then yield a sublimate of the acid, and leave a mixture of a monobasic salt, and a brown bibasic salt containing 31·93 p. c. strontia, which detonates with great violence. The monobasic salt detonates sharply, and in the dark with a dazzling purple flame. It dissolves easily in cold, very easily in boiling water, and very slowly in boiling absolute alcohol, which renders the crystals turbid by extracting water from them.— *Picranisate of Strontia:* Yellow, sparingly soluble, slender needles, having a silky lustre. (Cahours.)

| | Crystals. | | Marchand. |
|---|---|---|---|
| $C^{12}N^3H^2O^{13}$ | 220 | 69·40 | |
| SrO | 52 | 16·40 | 16·43 |
| 5 HO | 45 | 14·20 | |
| $C^{12}N^3H^2SrO^{14} + 5Aq$ | 317 | 100·00 | |

*Picrate of Lime.*—Obtained by dissolving carbonate of lime in the aqueous acid. Smooth four-sided prisms, which detonate when heated like the potash-salt, and dissolve readily in water. (Liebig.) The crystals contain 9·56 p. c. lime, and therefore 5 At. water. When moderately heated, they likewise yield a basic salt. They dissolve in water even more readily than the baryta or the strontia-salt. (Marchand.)

*Picrate of Magnesia.*— Very long, slender, flat needles of a light yellow colour, detonating very strongly when heated (after giving off water, according to Marchand), easily soluble in water. (Liebig.) They appear to contain 5 At. water. They dissolve in water still more readily than the lime-salt, but are nearly insoluble in boiling alcohol which abstracts their water of crystallisation. (Marchand.)

Picric acid forms white scales with hydrochlorate of *alumina* and with *tartar-emetic.* (Moretti.)

*Picrate of Manganese.* — The brown crystals appears to contain 8 At. water, 3 At. of which escape rapidly in the air, so that the air-dried salt contains 11·8 p. c. protoxide of manganese and 5 At. water, 4 At. of which it gives off at 130°. (Marchand.)

| | Dried at 130°. | | Marchand. |
|---|---|---|---|
| 12 C | 72 | 27·17 | 27·19 |
| 3 N | 42 | 15·85 | |
| 3 H | 3 | 1·13 | 1·40 |
| MnO | 36 | 13·59 | 13·50 |
| 14 O | 112 | 42·26 | |
| $C^{12}N^3H^2MnO^{14} + Aq$ | 265 | 100·00 | |

*Picrate of Zinc.*— The beautiful yellow transparent crystals belonging to the right prismatic system, which effloresce quickly, give off 8·0 p. c. (3 At.) water in dry air, 9·3 p. c. altogether at 100°, and 17·24 p. c. altogether (nearly 7 At.) at 140°, at which temperature however, a small quantity of acid likewise goes off; and leave a salt which contains 14·33 p. c. zinc-oxide, therefore still retains 1 At. water, and when more strongly heated, swells up, gives off water and acid, and finally detonates moderately but with a bright flame. In the flame of a candle, the salt takes fire, flying about quickly in fiery flakes, and giving off a thick black smoke. The salt dried at 140°, melts in boiling water to a brown liquid, which when stirred about, absorbs water and solidifies in a yellow crystalline mass. The salt dissolves abundantly in alcohol, and on subsequent evaporation, forms a thick syrup, which when agitated in the cold, solidifies to a mass of needles. (Marchand.)

| *Dried in vacuo.* | | | Marchand. |
|---|---|---|---|
| 12 C | 72·0 | 23·59 | 23·30 |
| 3 N | 42·0 | 13·76 | |
| 7 H | 7·0 | 2·30 | 2·52 |
| ZnO | 40·2 | 13·17 | 13·57 |
| 18 O | 144·0 | 47·18 | |
| $C^{12}N^3H^2ZnO^{14}$ + 5Aq. | 305·2 | 100·00 | |

*Picrate of Lead.*—*a. Quintobasic.*—Formed by precipitating a boiling dilute solution of neutral acetate of lead with picrate of ammonia strongly supersaturated with ammonia. The dark yellow powder, when examined by the microscope, appears to consist of rectangular tables, mixed however with a few colourless crystals. (Laurent.) When heated, it burns without detonation, but with projection, and leaves suboxide of lead, which changes to protoxide on exposure to the air. (Marchand.)

| | | | Laurent. | Marchand at 100°. |
|---|---|---|---|---|
| 12 C | 72 | 9·23 | | 9·92 |
| 3 N | 42 | 5·38 | | |
| 2 H | 2 | 0·26 | | 0·52 |
| 5 PbO | 560 | 71·80 | 69·67 | 70·92 |
| 13 O | 104 | 13·33 | | |
| 4PbO + $C^{12}N^3H^2PbO^{14}$ | 780 | 100·00 | | |

*b. Terbasic.* — *α. Anhydrous.*—From a solution of neutral acetate of lead mixed with a little ammonia, a concentrated solution of picrate of potash throws down during ebullition, a yellowish red crystalline powder, which is nearly insoluble in water even at the boiling heat, does not give off quite 1 p. c. water at 130°, and detonates with violence at a stronger heat, as also under the hammer. (Marchand.)

*β. Hydrated.*— A mixture of picrate of ammonia and slightly acidulated acetate of lead yields on addition of ammonia, a light yellow precipitate, which crystallises on standing in small shining scales unctuous to the touch, which detonate at 200°, and with difficulty by percussion. (Marchand.) To this place belongs perhaps the precipitate which Laurent obtained in yellow strongly detonating flakes by mixing picrate of ammonia with basic acetate of lead.

| *α*. at 130°. | | | Marchand. |
|---|---|---|---|
| 12 C | 72 | 12·95 | |
| 3 N | 42 | 7·55 | |
| 2 H | 2 | 0·36 | |
| 3 PbO | 336 | 60·43 | 59·64 |
| 13 O | 104 | 18·71 | |
| $2PbO,C^{12}N^3H^2PbO^{14}$ | 556 | 100·00 | |

| *β*. at 100°. | | | Marchand. |
|---|---|---|---|
| 12 C | 72 | 12·35 | 12·73 |
| 3 N | 42 | 7·20 | |
| 5 H | 5 | 0·86 | 0·81 |
| 3 PbO | 336 | 57·63 | 57·20 |
| 16 O | 128 | 21·96 | |
| $2PO,C^{12}N^3H^2PbO^{14}+3Aq$ | 583 | 100·00 | |

Marchand distinguishes also a light yellow $\frac{5}{2}$-basic salt containing 52·33 p.c. (5 At.) oxide and 6·51 (8 At.) water, which detonates violently even at 180°.

*c. Bibasic.*—1. A boiling dilute mixture of picrate of ammonia and neutral acetate of lead deposits at first heavy crystals of the salt *c*, then lighter, pale yellow, shining laminæ of a sesquibasic salt [or perhaps of the salt containing acetic acid] which may for the most part be separated by elutriation. Dark yellow microscopic rhombic tables which give off 1·6 p.c. water at 100°, and detonate with violence when struck. (Laurent.)—2. When neutral acetate of lead is precipitated in the cold by picrate of ammonia, yellow, shining, micaceous scales are obtained which detonate violently when struck or heated. (Marchand.)

| *Air-dried.* | | | Laurent. | Marchand. |
|---|---|---|---|---|
| $C^{12}N^3H^2O^{13}$ | 220 | 48·56 | | |
| 2 PbO | 224 | 49·45 | 45·07 | 49·48 |
| HO | 9 | 1·99 | 1·60 | |
| $PbO,C^{12}N^3H^2PbO^{14}+Aq$ | 453 | 100·00 | | |

The deficiency in the lead-oxide arose from admixture of the lighter salt. (Laurent.)

*d. Monobasic.*—The hot mixture of an alkaline picrate and slightly acidulated acetate of lead [not in excess ?], yields on cooling, brown needles which detonate with violence and dissolve pretty easily in water. (E. Kopp, *N. Ann. Chim. Phys.* 13, 233.) Aqueous picric acid saturated while hot with carbonate of lead, yields detonating needles sparingly soluble in water. (Chevreul.)

| *Needles.* | | | E. Kopp. |
|---|---|---|---|
| $C^{12}N^3H^2O^{13}$ | 220 | 64·51 | 64·70 |
| PbO | 112 | 32·85 | 32·76 |
| HO | 9 | 2·64 | 2·54 |
| $C^{12}N^3H^2PbO^{14}$ + Aq | 341 | 100·00 | 100·00 |

*Picracetate of Lead.*—The hot aqueous mixture of picrate of potash and excess of acetate of lead yields on cooling, and by further evaporation and cooling of the mother-liquor, light yellow, highly lustrous

rhombic laminæ. The crystals have an acid reaction, exhale nearly all the acetic acid even at ordinary temperatures after drying, and are converted into a yellow nearly insoluble powder containing scarcely any acetic acid, whereas they previously dissolved with facility. (E. Robiquet, *N. J. Pharm.* 14, 179.) They give off 4·37 p. c. water (and acetic acid) at 180°, and when treated with sulphuric acid, evolve acetic acid. (Marchand.) Their aqueous solution is resolved by evaporation into yellow, pulverulent picrate of lead (which dissolves in a large quantity of boiling water and likewise in acetate of lead), and crystallises therefrom in laminæ, and acetate of lead which remains in solution. (Schunck, Marchand.) If the acetic acid be replaced as it evaporates during the boiling down of the solution, the residue when tolerably concentrated, yields brown scales having a metallic lustre, and probably consisting of neutral picrate of lead. (Schunck.)

The pale yellow, shining laminæ obtained by Laurent (p. 244), which were doubtless identical with this salt, but in which he did not look for acetic acid, give off 3·6 p. c. water in vacuo at 110°, contain 42·08 p. c. lead-oxide, and detonate by percussion.

| *Dried.* | | | Schunck, *at* 100°. | Marchand, *at* 180°. | Robiquet, *by time.* |
|---|---|---|---|---|---|
| 16 C | 96 | 19·40 | 17·42 | 18·33 | 20·82 |
| 3 N | 42 | 8·49 | 8·64 | | 7·32 |
| 5 H | 5 | 1·01 | 1·07 | 1·34 | 1·12 |
| 2 PbO | 224 | 45·25 | 47·56 | 45·88 | 40·76 |
| 16 O | 128 | 25·85 | 25·31 | | 29·98 |
| $C^{12}N^3H^2PbO^{14} + C^4H^3PbO^4$ | 495 | 100·00 | 100·00 | | 100·00 |

If the recent crystals contained 2 At. water, they would give off 3·51 p. c. in drying. According to Schunck, the dry salt is $3PbO,2C^{12}N^3H^2O^{13} + PbO,C^4H^3O^3$; according to Marchand, the same + 4Aq; according to Robiquet, about $2\frac{1}{2}PbO,C^{12}N^3H^2O^{13},3C^4H^3O^3$.

From aqueous chloride of iron, picric acid throws down white scales (Moretti); it does not redden ferric salts. (Liebig.)

*Picrate of Cobalt.*—By dissolving carbonate of cobalt in the boiling aqueous acid, evaporating, dissolving the dry residue in boiling absolute alcohol, and recrystallising from water the crystals which separate from the filtrate, dark brown needles are obtained, which melt and give off the whole of their water of crystallisation, amounting to 14·4 p. c. (5 At.) between 100° and 110°, and at a stronger heat, decompose suddenly with a hissing noise and a dazzling white light, the mass being scattered about in all directions. (Marchand.)

| *Crystals.* | | | Marchand. |
|---|---|---|---|
| 12 C | 72·0 | 23·80 | 24·46 |
| 3 N | 42·0 | 13·88 | |
| 7 H | 7·0 | 2·32 | 2·66 |
| CoO | 37·5 | 12·40 | 12·17 |
| 18 O | 144·0 | 47·60 | |
| $C^{12}N^3H^2CoO^{14} + 5Aq.$ | 302·5 | 100·00 | |

*Picrate of Nickel.*—A solution of carbonate of nickel in the acid, abandoned to spontaneous evaporation, deposits in the middle of the basin,

green transparent shining crystals exhibiting a dichroism similar to that of uranic salts, and at the edge, brown dendritic efflorescences. The green crystals, which contain 8 At. water, quickly effloresce on exposure to the air, and are converted into the brown salt (containing 5 At. water); over oil of vitriol they soon give off 7·6 p. c. (3 At.) water. The same brown salt separates from the alcoholic solution on evaporation, in dark brown crystals which yield a light brown powder. It gives off at 130°, 11·72 p. c. (4 At.) water, and between 160° and 180°, water containing acid, melting at the same time and being converted into a basic salt, which at a stronger heat, explodes with some violence and with a dazzling white flame. The salt dissolves easily in water and alcohol, and the alcoholic solution, when rapidly evaporated to dryness, leaves a greenish brown varnish, which forms a brown crystalline mass with a comparatively small quantity, and a green crystalline mass with a larger quantity of water. (Marchand.)

| *Dried at* 100°. | | | Marchand. |
|---|---|---|---|
| 12 C | 72·0 | 27·02 | 27·30 |
| 3 N | 42·0 | 15·76 | |
| 3 H | 3·0 | 1·12 | 1·50 |
| NiO | 37·5 | 14·07 | 14·13 |
| 14 O | 112·0 | 42·03 | |
| $C^{12}N^3H^2NiO^{14}$ + Aq | 266·5 | 100·00 | |

*Picrate of Copper.* — By precipitating picrate of baryta with sulphate of copper and evaporating the filtrate, green fern-like laminæ are obtained, which do not detonate or take fire when heated, deliquesce in the air, and dissolve in 1 pt. of water. (Liebig.) — 2. The greenish brown solution of carbonate of copper in the boiling acid leaves on evaporation a crystalline mixture of a basic salt, soluble in water but not in alcohol, and a neutral salt which may be dissolved out by boiling alcohol. This solution evaporated at a gentle heat to the crystallising point, yields small green shining needles, and a mother-liquor, which, after evaporation to a sprup, solidifies on being stirred. — The crystals effloresce in the air: they melt at 110°, giving off 11·44 p. c. (3 At.) water, and form a brown mass, which at 150°, gives off 4 or 5 p. c. more water together with picric acid, so that it is afterwards mixed with a still more basic salt. Finally, a slight explosion takes place, accompanied by a dark red flame and a large quantity of smoke containing nitrous acid, cyanogen, hydrocyanic acid, and perhaps also Boutin's cyanyl. (Marchand.)

| *Crystals.* | | | Marchand. |
|---|---|---|---|
| 12 C | 72 | 23·61 | 24·31 |
| 3 N | 42 | 13·77 | |
| 7 H | 7 | 2·30 | 2·50 |
| CuO | 40 | 13·11 | 13·29 |
| 18 O | 144 | 47·21 | |
| $C^{12}N^3H^2CuO^{14}$ + 5Aq | 305 | 100·00 | |

*Mercurous Picrate.*—Separates on cooling from a hot aqueous mixture of the potash-salt and mercurous nitrate, in small yellow four-sided prisms (according to Moretti, in white scales). Does not detonate when heated, but burns away like gunpowder. Requires more than 1200 pts. of cold water to dissolve it. (Liebig.)

| | | | | Liebig. |
|---|---|---|---|---|
| $C^{12}N^3H^2O^{13}$ | 220 | 51·40 | | |
| $Hg^2O$ | 208 | 48·60 | | 46·21 |
| $C^{12}N^3H^2Hg^2O^{14}$ | 428 | 100·00 | | |

*Mercuric Picrate.*— By dissolving mercuric oxide in the aqueous acid, a compound is obtained which detonates when heated. (Chevreul.)

*Picrate of Silver.* — The solution of oxide of silver in the aqueous acid, or a mixture of aqueous nitrate of silver with the acid or its potash-salt, is evaporated at a gentle heat and left to cool. Beautiful, yellow, shining needles united in radiated groups. (Chevreul, Liebig.) The salt blackens on exposure to the air (and light ?) and detonates when heated. (Chevreul.) When heated it burns without detonation, like gunpowder. Dissolves readily in water. (Liebig.) *Chrysolepate of silver* :— Brown-red needles (Schunck); *Picranisate of silver* : Orange-yellow needles. (Cahours.)

| | | | Dumas. | Marchand. |
|---|---|---|---|---|
| 12 C | 72 | 21·43 | 21·35 | |
| 3 N | 42 | 12·50 | | |
| 2 H | 2 | 0·60 | 0·97 | |
| Ag | 108 | 32·14 | 31·80 | 31·9 |
| 14 O | 112 | 33·33 | | |
| $C^{12}N^3H^2AgO^{14}$ | 336 | 100·00 | | |

Hence, according to Laurent, the needles give off 2·2 to 3 p. c. at 100° in vacuo, and according to Marchand, they give up 3·1 p. c.; these chemists suppose them to contain 1 At. water.

Picric acid dissolves readily in *alcohol* and in *ether*. (Liebig, Schunck, Cahours.)

It dissolves sparingly in cold *creosote*, but very abundantly in the same liquid when hot, forming a yellow solution from which it does not separate on cooling. (Reichenbach.)

It precipitates gelatin. (Chevreul.) — It imparts a permanent yellow tinge to cloth-stuffs, &c. ¶. According to J. J. Pohl, (*Wien. akad. Ber.* 9, 386), this character may serve to distinguish between animal and vegetable tissues, only the former being coloured yellow by picric acid. — The presence of picric acid in beer (in which it is said to be sometimes introduced as a substitute for hops) may be detected even to the amount of $\frac{1}{125000}$, by boiling a piece of unbleached sheep's wool for 6 to 10 minutes in the suspected liquid, and then washing it: if picric acid be present, the wool assumes a canary-yellow colour. (Pohl, *Wien. Akad. Ber.* 12, 88.) ¶.

## Picric Ether.

A solution of picric acid in absolute alcohol mixed with a little oil of vitriol, is boiled for some hours in a flask having an ascending condensing tube attached to it, so that the alcohol may continually run back; and the

liquid is mixed with ammonia, and afterwards with water which separates the ether. — Erdmann (*J. pr. Chem.* 37, 413) did not succeed in preparing picric ether by this process.

Yellowish laminæ, which melt at 91° and boil with decomposition at 300°. Inodorous, but has a burning bitter taste.

Sparingly soluble in cold, more easily in boiling water. (Mitscherlich, *Lehrb. der Chemie*, 1, 222; *J. pr. Chem.* 22, 195.)

[This is the only instance yet known of the production of a compound ether from an acid aldide (containing 2 O outside the nucleus)].

¶. *Appendix to Picric Acid.*

## Ternitrocresylic Acid.

$C^{14}N^3H^5O^{14} = C^{14}X^3H^5,O^2$.

When fuming nitric acid is added by small portions to creosote (containing $C^{14}H^8O^2$) in a vessel surrounded with ice, the colour of the liquid gradually changes to deep red, and after the addition of a volume of nitric acid about equal to that of the creosote, the liquid separates into two layers, the upper of a deep red colour, the lower black and tarry. The upper portion neutralised with potash, solidified into a distinctly crystalline mass sparingly soluble in cold but readily in hot water. (Fairlie, *Chem. Soc. Qu. J.* 7, 236.)

| | | | Fairlie. |
|---|---|---|---|
| $C^{14}N^3H^4O^{13}$ | 234·0 | 83·25 | |
| KO | 47·2 | 16·75 | 17·08 |
| $C^{14}N^3H^4KO^{14}$ | 281·2 | 100·00 | |

An attempt was made to obtain a substitution product containing only 1 or 2 At. $NO^4$, by acting with dilute nitric acid on an alcoholic solution of creosote previously mixed with nitrate of urea; but no definite result was obtained. (Fairlie.) ¶.

## Styphnic Acid.

$C^{12}N^3H^3O^{16} = C^{12}X^3H^3,O^4$.

Chevreul. *Ann. Chim.* 66, 216; 73, 43; the latter also in *Gilb.* 44, 128.
Erdmann. *J. pr. Chem.* 37, 409; 38, 355.
R. Böttger and H. Will. *Ann. Pharm.* 58, 273.
Fred. Rothe. *J. pr. Chem.* 46, 376.

From στύφνος astringent. — *Oxypicric acid* (Erdmann); *artificial bitter* or *artificial tannin of extract of logwood.* (Chevreul.)—First obtained in an impure state by Chevreul in 1808; in the pure state, and more precisely investigated, by Erdmann in 1846, and a few weeks later by Böttger & Will.

*Formation.* By continued boiling of extract of logwood (Chevreul), euxanthone (Erdmann), gum-ammoniacum, asafœtida, galbanum, sagape-

num, or the watery extract of fustic or sandal-wood (Böttger & Will), or peucedanin (Rothe) with nitric acid.

*Preparation.* 1. *From Asafœtida.* 1 pt. of asafœtida in lumps of the size of a walnut, is heated to a temperature between 70° and 75° in a wide porcelain basin, with 4 to 6 pts. of nitric acid of sp. gr. 1·2, free from sulphuric and hydrochloric acid; and, after the resin has become soft and divided, and a thick froth has risen,—which must be prevented from running over by stirring—the mass, which is then lemon-coloured and viscid, is kept, together with the surrounding nitric acid liquid, at the boiling heat, with frequent addition of fresh acid, till (in 5 or 6 hours) it is completely dissolved; the dark red-brown solution, is then evaporated nearly to a syrup and mixed with a small quantity of water. If after this it gives a greasy resinous precipitate, it must be boiled for a longer time with nitric acid; but if it gives a yellowish sandy precipitate, it must be carefully evaporated to a thick syrup to drive off the greater part of the nitric acid; then heated to the boiling point with a tolerably large quantity of water; mixed with carbonate of potash as long as effervescence ensues, but no longer (so as not to redissolve any undecomposed portion of the resin which rises to the surface when the liquid is neutralised); strained through grey paper; evaporated, and left to crystallise. The mother-liquor repeatedly evaporated and cooled yields an additional quantity of crystals of impure styphnate of potash, till at last nitrate of potash (but no oxalate) separates out. The needle-shaped crystals, united in red-brown crusts and nodules, are freed from the mother-liquor by draining on bibulous paper; twice recrystallised from water, with addition of animal charcoal; then dissolved in the smallest possible quantity of boiling water; nitric acid added; and the styphnic acid, which separates after complete cooling as a yellowish white powder, or in fern-like laminæ, collected on a filter, washed several times with cold water, and after thorough drying, recrystallised from boiling absolute alcohol. The process yields 3 per cent. of styphnic acid. (Böttger & Will.)

*From commercial extract of Logwood.* 1 pt. of the extract is added to 4 or 6 pts. of nitric acid of sp. gr. 1·37, heated to 40° in a capacious dish; and as soon as the first violent action is over, the dark, red-brown liquid is continuously heated, with occasional addition of fresh acid, till the evaporated liquid, when mixed with water, begins to deposit styphnic acid in the form of a sandy powder. It is then left to cool; the mother-liquor decanted from the precipitated styphnic acid; this acid boiled with nitric acid, &c., &c., as long as styphnic acid can be obtained from it, and the product purified in the same manner as that obtained from asafœtida. In this manner, 18·5 p. c. acid is obtained. (Böttger & Will.) — 1 pt. of the extract is boiled to dryness with 5 pts. of nitric acid of 32° Bm. and 2 pts. of water; the residue dissolved in boiling water; filtered hot from sand, &c.; and the flakes which fall down as the liquid cools, washed with cold water, dissolved in hot water, and filtered from the artificial orange-yellow resin. The acid is then obtained on cooling, in the form of a yellowish white, non-crystalline precipitate, still contaminated with a small quantity of orange-yellow resin. (Chevreul.)

The *artificial orange-yellow resin of extract of logwood*, the formation of which has just been described [which would probably be converted into styphnic acid by further boiling with nitric acid], is orange-yellow, sometimes granular, tastes slightly rough, does not redden litmus, becomes

charred on red-hot iron, and then deflagrates. It dissolves sparingly in cold water, more freely in hot water, forming a yellow solution which becomes turbid on cooling, is precipitated by sulphuric, hydrochloric or nitric acid, and by protochloride of tin, acetate of lead, ferric sulphate (in red flakes) or nitrate of silver, and immediately coagulates a solution of gelatin. (Chevreul.)

3. *From Euxanthone or Euxanthic acid.* These substances are boiled for some time with nitric acid of sp. gr. 1·31; the solution evaporated over the water-bath, below 100° towards the end, as otherwise the nitric acid would completely convert the styphnic acid into oxalic acid [in presence of hydrochloric acid?]; the sparingly soluble styphnic acid separated from the oxalic acid by repeated crystallisation, and dissolved in dilute carbonate of ammonia; this solution saturated while warm with carbonate of ammonia, whereby the styphnate of ammonia, which is insoluble in aqueous carbonate of ammonia, is made to crystallise in yellow four-sided prisms; these crystals, if too dark-coloured, purified by animal charcoal; and the styphnic acid separated from them by hydrochloric acid.

4. *From Peucedanin.* The styphnic acid obtained by treating peucedanin with warm nitric acid, is mixed with potash to free it from the oxalic acid which is abundantly mixed with it; the styphnate of potash which crystallises out, washed with cold water; its solution in hot water precipitated by a lead-salt; and the acid separated from the precipitate. (Rothe.)

*Properties.* Pale yellow, regular, six-sided prisms having the habit of green lead ore; they grate between the teeth, melt when carefully heated, and solidify in the radiated form on cooling (Böttger & Will); pale yellow or colourless needles or four-sided tables, which are fusible, sublime partly without decomposition, and likewise evaporate with the water when their aqueous solution is boiled (Erdmann); nearly colourless tables. (Rothe.) The acid has a slightly rough taste, neither bitter nor sour, but reddens litmus strongly, and when dissolved in alcohol, colours the skin permanently yellow (Böttger & Will); rough and leaving a persistent, irritating, and bitter after-taste. (Erdmann.) — Yellow, tastes somewhat sour, afterwards very rough and bitter. (Chevreul.)

| | *Crystals.* | | Böttger & Will. | Erdmann. |
|---|---|---|---|---|
| 12 C | 72 | 29·39 | 29·15 | 29·62 |
| 3 N | 42 | 17·14 | 16·97 | 17·30 |
| 3 H | 3 | 1·23 | 1·55 | 1·30 |
| 16 O | 128 | 52·24 | 52·33 | 51·78 |
| $C^{12}N^3H^3O^{16}$ | 245 | 100·00 | 100·00 | 100·00 |

The crystals do not give off anything between 100° and 150°. (Böttger & Will.)

*Decompositions.* 1. The acid heated somewhat above its melting point, gives off vapours which are set on fire by contact with a flaming body. When suddenly heated, it deflagrates like gunpowder, with a bright yellow flame, mostly bordered with orange-yellow. (Böttger & Will.) Leaves a residue of charcoal. (Erdmann.) When gradually heated, it gives off nitrous gas, nitrogen, carbonic acid, inflammable gas and water, and leaves very finely-divided charcoal; on red-hot iron it deflagrates with flame. (Chevreul.) 2. It is completely destroyed by boiling *nitro-hydrochloric acid,* with formation of oxalic acid, whereas boiling con-

centrated nitric or hydrochloric acid alone has no action upon it. (Böttger & Will.) — 3. It is decomposed by boiling *oil of vitriol.* (Böttger & Will.) — It is not decomposed by boiling with excess of concentrated potash; and when digested with lime and protosulphate of iron, does not form a red liquid as picric acid does, but a colourless liquid. (Erdmann.) — 4. It is not altered by sulphuretted hydrogen; but the light yellow mixture of the acid dissolved in alcohol with hydrosulphate of ammonia, immediately acquires a dark brown-red colour when heated, and leaves on evaporation a black mass, containing, besides sulphur and a small quantity of black powder, an ammonia-salt which may be dissolved out by water, and whose acid resembles picric acid and styphnic acid. — 5. The hot aqueous acid dissolves protosulphide of iron with less evolution of sulphuretted hydrogen than might be expected. With zinc or iron, it likewise gives off a less than proportionate quantity of hydrogen, forming greenish brown solutions. It does not act on cadmium, lead, copper or silver. — Its powder strewn on potassium (not on sodium) takes fire when slightly pressed with a pestle. (Böttger & Will.)

*Combinations.* The acid dissolves with yellow colour in 104 pts. of water at 25° (Erdmann), and in 88 pts. at 62° (Böttger & Will.)

It dissolves abundantly in strong *nitric acid,* less in strong *hydrochloric acid,* and is partially precipitated from both acids by water in the form of a powder. (Böttger & Will.)

The acid easily decomposes carbonates. It takes up, for 1 At. HO, 2 At. of base of the same or different kinds, forming bibasic simple and double salts which are neutral. (Böttger & Will.) Nearly all *styphnates* detonate, when subjected to a gradually increasing heat (not by percussion), even more violently than the picrates. (Böttger and Will, Erdmann.) From the aqueous solutions of the heavy metallic salts of this acid, animal charcoal removes the whole of the oxide, especially from the styphnates of manganese, lead, nickel and copper. (Böttger & Will, Rothe.)

*Styphnate of Ammonia.* — *a. Bibasic.* The aqueous acid neutralised with ammonia (and then saturated, while warm, with solid carbonate of ammonia, which diminishes the solubility of styphnate of ammonia in water: *Erdmann*), yields large orange-yellow needles (yellow four-sided prisms, according to Erdmann) which detonate slightly when heated, and dissolve in water more readily than the salt *b.*

| *Crystals.* | | | Erdmann. | Böttger & Will. | Rothe. |
|---|---|---|---|---|---|
| 12 C | 72 | 25·81 | 25·89 | 25·48 | 25·68 |
| 5 N | 70 | 25·09 | 25·09 | 24·89 | |
| 9 H | 9 | 3·23 | 3·22 | 3·37 | 3·41 |
| 16 O | 128 | 45·87 | 45·80 | 46·26 | |
| $NH^3,C^{12}N^3H^2(NH^4)O^{16}$. | 279 | 100·00 | 100·00 | 100·00 | |

*b. Monobasic.* — Obtained by neutralising one-half of the acid with carbonate of ammonia, adding the other half, and then evaporating and cooling. A comparatively dilute solution yields large, light yellow, flat needles, and a solution more concentrated by evaporation yields capillary interlaced needles, which detonate very slightly. (Böttger & Will.)

| *Crystals.* | | | Böttger & Will. |
|---|---|---|---|
| 12 C | 72 | 27·48 | 27·58 |
| 4 N | 56 | 21·37 | 21·52 |
| 6 H | 6 | 2·29 | 2·36 |
| 16 O | 128 | 48·86 | 48·54 |
| $C^{12}N^3H^2(NH^4)O^{16}$ | 262 | 100·00 | 100·00 |

*Styphnate of Potash.* — *a. Bibasic.* — The aqueous acid neutralised with carbonate of potash, yields by gentle evaporation and cooling, orange-yellow needles, often united in nodules, which are anhydrous and detonate with violence. (Böttger and Will.) Potash added in excess to the aqueous acid throws down a yellow crystalline powder, crystallising from hot water in dark yellow needles, which detonate strongly (according to Chevreul, with a long purple flame and formation of hydrocyanate of ammonia.) They dissolve at 23° in 58 pts. of pure water (Erdmann), much less freely in water containing potash or carbonate of potash. (Erdmann, Böttger & Will.)

| | | | Böttger & Will. |
|---|---|---|---|
| $C^{12}N^3H^2O^{15}$ | 236·0 | 71·43 | |
| 2 KO | 94·4 | 28·57 | 28·60 |
| $KO,C^{12}N^3H^2KO^{16}$ | 330·4 | 100·00 | |

*c. Monobasic.* — Prepared by neutralising one-half of the acid with carbonate of potash, and adding the other half. Light yellow, capillary, interlacing needles, which quickly change to a granular powder when dried on paper; a more dilute solution yields larger and more solid crystals. At 100°, they give off 6·4 p. c. (2 At.) water of crystallisation, and at a higher temperature part of the acid, whereupon violent detonation ensues. (Böttger & Will.)

| *Dried at* 100° | | | Böttger & Will. |
|---|---|---|---|
| 12 C | 72·0 | 25·42 | 25·15 |
| 3 N | 42·0 | 14·83 | |
| 2 H | 2·0 | 0·71 | 0·87 |
| KO | 47·2 | 16·67 | 16·40 |
| 15 O | 120·0 | 42·37 | |
| $C^{12}N^3H^2KO^{16}$ | 283·2 | 100·00 | |

*Styphnate of Soda.* — *Bibasic.* — Small, light yellow needles, often grouped in hard nodules; they give off 13·08 p. c. (5 At.) water at 100°, and detonate with great violence when slowly raised to a higher temperature; they dissolve readily in water. (Böttger & Will.)

The *monobasic salt* cannot be obtained in the crystalline form. (Böttger & Will.)

| *Dried at* 100°. | | | Böttger & Will. |
|---|---|---|---|
| $C^{12}N^3H^2O^{15}$ | 236·0 | 79·09 | |
| 2 NaO | 62·4 | 20·91 | 20·71 |
| $NaO,C^{12}N^3H^2NaO^{16}$ | 298·4 | 100·00 | |

*Styphnate of Baryta.* — *Bibasic.* — Obtained by saturating the aqueous solution with carbonate of baryta. Short, slender, orange-yellow needles.

They give off 4·08 p. c. (2 At.) water at 100°, leaving 2 At. and detonate with great violence when gradually raised to a higher temperature. After the lead-salt, this is the least soluble of the styphnates. (Böttger & Will.)

| | *Dried at* 100°. | | | Böttger & Will. | Erdmann, at 120°. |
|---|---|---|---|---|---|
| $C^{12}N^3H^4O^{17}$ | 254·0 | .... | 62·38 | | |
| 2 BaO | 153·2 | .... | 37·62 | 37·59 | 38·59 |
| $BaO,C^{12}N^3H^2BaO^{16}$ + Aq | 407·2 | .... | 100·00 | | |

*Styphnate of Strontia.* — *Bibasic.* — Large nodules composed of slender light yellow needles containing 4 At. water, of which 7·02 p. c. (3 At.) go off at 100°; they dissolve in water more readily than the baryta-salt. (Böttger & Will.)

| | *Dried at* 100°. | | | Böttger & Will. |
|---|---|---|---|---|
| $C^{12}N^3H^3O^{16}$ | 245 | .... | 70·20 | |
| 2 SrO | 104 | .... | 29·80 | 29·48 |
| $SrO,C^{12}N^3H^2SrO^{16}$ + Aq | 349 | .... | 100·00 | |

*Styphnate of Lime.* — *Bibasic.* — The light yellow needles grouped in nodules give off 10·22 p. c. (4 At.) water at 100°, and retain 3 At. (Böttger & Will.)

| | *Dried at* 100°. | | | Böttger & Will. |
|---|---|---|---|---|
| 12 C | 72 | .... | 22·57 | 22·31 |
| 2 N | 28 | .... | 13·17 | |
| 5 H | 5 | .... | 1·57 | 1·77 |
| 2 CaO | 56 | .... | 17·55 | 17·61 |
| 18 O | 144 | .... | 45·14 | |
| $CaO,C^{12}N^3H^2CaO^{16}$ + 3Aq | 319 | .... | 100·00 | |

*Styphnate of Magnesia.* — Crystallises with difficulty in light yellow nodules, which give off 9·1 p. c. water at 100°. Detonates violently when slowly heated. (Böttger & Will.)

*Styphnate of Manganese.* — *Monobasic.* — Obtained, by precipitating the baryta-salt with sulphate of manganese, and evaporating the filtrate, in large, light yellow, rhombic tables belonging to the doubly oblique prismatic system which melt and redden at 100°, giving off 22·98 p. c. (10 At.) water (while 2 At. remain together with 12·29 p.c. manganous oxide) and then deflagrate at a stronger heat. (Böttger & Will.)

*Styphnate of Zinc.* — *With 5 At. base to 2 At. acid ?* The aqueous acid saturated with carbonate of zinc, and ultimately evaporated over oil of vitriol, crystallises with difficulty in very deliquescent needles grouped in nodules. These crystals give off 3·78 p. c. water at 100°, and the residue, which detonates slightly when heated, contains 28·32 p. c. zinc-oxide. (Böttger & Will.)

*Styphnate of Cadmium.* — Slightly detonating; deliquescent. (Böttger & Will.)

*Styphnate of Lead.* — *Quadrobasic.* — The light yellow flakes precipitated by the free acid from acetate of lead, detonate violently by strong pressure and are scarcely soluble in water. (Böttger & Will.) The ammonia-salt forms a similar precipitate with acetate of lead in the cold, and small yellow needles from hot solutions. (Erdmann.)

| *Dried at* 100°. | | | | Böttger & Will. | Erdmann. |
|---|---|---|---|---|---|
| 12 C | 72 | .... | 10·26 | ........ 10·32 | |
| 3 N | 42 | .... | 5·98 | | |
| 4 H | 4 | .... | 0·57 | ........ 0·63 | |
| 4 PbO | 448 | .... | 63·82 | ........ 63·68 | .... 63·62 |
| 17 O | 136 | .... | 19·37 | | |
| $3PbO,C^{12}N^3H^2PbO^{16} + 2Aq$ | 702 | .... | 100·00 | | |

*Ferrous Styphnate.* — The filtrate obtained by precipitating the baryta-salt with ferrous sulphate, slowly yields black-green crystals which dissolve readily and pass to a higher state of oxidation. (Böttger & Will.)

*Ferric Styphnate.* — The ammonia-salt mixed with iron-alum forms yellow needles. (Erdmann.)

*Styphnate of Cobalt.* — The light brown, violently detonating, and easily soluble needles united in nodules, give off 9·28 p. c. of water at 100°, and leave a salt containing 21·44 p. c. of protoxide of cobalt. (Böttger & Will.)

*Styphnate of Cobalt and Ammonium.* — Brownish yellow needles. (Böttger & Will.)

*Styphnate of Cobalt and Potassium.* — Hard brown crystalline nodules containing 11·7 p. c. oxide of cobalt, and not giving off any thing at 100°. (Böttger & Will.)

*Styphnate of Nickel.* — Crystallises with difficulty in light yellow needles, which detonate with violence and dissolve very readily. (Böttger & Will.)

*Styphnate of Nickel and Potassium.* — Brown crystalline crusts. Detonates with tremendous violence when heated; contains 10·32 p. c. oxide of nickel, and does not suffer any loss at 100°. (Böttger & Will.)

*Styphnate of Copper.* — The evaporated dark brown solution of carbonate of copper in the aqueous acid deposits, after a few days, long light green needles, which give off 13·81 p. c. (6 At.) water at 100°, and detonate with great violence at a stronger heat. (Böttger & Will.) Greyish yellow laminæ. (Erdmann.)

| | | | | Böttger & Will. |
|---|---|---|---|---|
| 12 C | 72 | .... | 21·56 | ........ 21·90 |
| 3 N | 42 | .... | 12·57 | |
| 4 H | 4 | .... | 1·20 | ........ 1·57 |
| 2 CuO | 80 | .... | 23·95 | ........ 23·12 |
| 17 O | 136 | .... | 40·72 | |
| $CuO,C^{12}N^3H^2CuO^{16} + 2Aq$ | 334 | .... | 100·00 | |

*Styphnate of Copper and Ammonium.* — Obtained by dissolving carbonate of copper in the saturated solution of monobasic styphnate of

ammonia. Short, thick, brown crystals which give off 15·47 p. c. (6 At.) water at 100°, deflagrate when heated, and dissolve with tolerable facility. (Böttger & Will.)

*Styphnate of Copper and Potassium.* — Prepared in like manner with the potash-salt. Brown hard needles, generally grouped in nodules. They give off 7·20 p. c. (3 At.) water at 100°, and detonate with tremendous violence when strongly heated. (Böttger & Will.)

| *Dried at* 100°. | | | | Böttger & Will. |
|---|---|---|---|---|
| $C^{12}N^3H^3O^{16}$ | 245·0 | .... | 73·75 | |
| KO | 47·2 | .... | 14·21 | |
| CuO | 40·0 | .... | 12·04 | ........ 12·01 |
| $CuO,C^{12}N^3H^2KO^{16} + Aq$ | 332·2 | .... | 100·00 | |

*Styphnate of Silver.* — *Bibasic.* The solution of carbonate of silver in the aqueous acid at 60°, or the mixture of the potash salt with a moderately strong solution of nitrate of silver prepared at 60° yields, when somewhat quickly cooled, light yellow, flat needles, 3 inches long, or by slow cooling, laminæ which dissolve sparingly in water, and from whose solutions, the silver is reduced on boiling with decomposition of the acid. (Böttger & Will.)

| *Dried at* 100°. | | | | Böttger & Will. | Erdmann. | Rothe. |
|---|---|---|---|---|---|---|
| 12 C | 72 | .... | 15·38 | ........ 15·04 | | |
| 3 N | 42 | .... | 8·98 | | | |
| 2 H | 2 | .... | 0·43 | ........ 0·86 | | |
| 2 AgO | 232 | .... | 49·57 | ........ 48·06 | .... 50·50 | .... 50·25 |
| 15 O | 120 | .... | 25·64 | | | |
| $AgO,C^{12}N^3H^2AgO^{16}$ | 468 | .... | 100·00 | | | |

Böttger & Will suppose the salt to contain 1 Aq in addition.

Styphnic acid dissolves readily in *alcohol* and *ether*, and more readily in strong *acetic acid* than in water. (Böttger & Will.)

It gives a copious precipitate with *gelatin*. (Chevreul.)

Erdmann (*J. pr. Chem.* 37, 413) did not succeed in preparing *styphnic ether* by heating styphnic acid with alcohol and oil of vitriol.

¶. *Nitrochlorine-nucleus* $C^{12}X^3H^2Cl$.

## Chloropicryl.

$$C^{12}N^3H^2ClO^{12} = C^{12}X^3H^2Cl.$$

PISANI. *Compt. rend.* 39, 852; *Ann. Pharm.* 92, 326.

This compound is obtained by the action of 1 At. pentachloride of phosphorus on 1 At. picric acid, oxychloride of phosphorus and hydrochloric acid being formed at the same time:

$$C^{12}X^3H^3O^2 + PCl^5 = C^{12}X^3H^2Cl + PCl^3O^2 + HCl.$$

The two bodies act violently on each other at first, and copious fumes of hydrochloric acid are evolved. As soon as this action ceases, and the oxychloride of phosphorus begins to pass over, the retort must be removed from the fire, because the chloropicryl would be decomposed by further heating, and a resinous substance formed; hence the chloropicryl cannot be completely purified from oxychloride of phosphorus by distillation.

Yellow, solid body, having an agreeable odour. Water decomposes it, forming hydrochloric and picric acids. Carbonate of ammonia converts it into picramide (p. 245). It dissolves in alcohol and in ether. (Pisani.)

### ¶. *Amidogen-nucleus* $C^{12}AdH^5$.

## Sulphophenylamide.

$$C^{12}NH^7S^2O^4 = C^{12}AdH^5,S^2O^4.$$

GERHARDT & CHANCEL. *Compt. rend.* 35, 690. — GERHARDT & CHIOZZA. *Compt. rend.* 37, 86.

*Azoture phenylsulfureux, Azoture de Sulfophényle et d'hydrogène.*

Formed by the action of ammonia on sulphite of chlorobenzene [or chloride of sulphophenyl $C^{12}H^5S^2O^4Cl$ (p.174)]. It is most conveniently prepared by pouring the latter compound upon a large excess of pulverised carbonate of ammonia. The action begins immediately, and may be completed by gently heating the mixture till the odour of the sulphate of chlorobenzene is no longer perceptible. The mass is then washed with cold water, to dissolve the hydrochlorate and carbonate of ammonia, and the residue crystallised from a small quantity of boiling alcohol.

Splendid nacreous scales, insoluble in water, easily soluble in alcohol, soluble also in ammonia.

*Calculation.*

| | | |
|---|---|---|
| 12 C | 72 | 45·86 |
| N | 14 | 8·92 |
| 7 H | 7 | 4·46 |
| 2 S | 32 | 20·38 |
| 4 O | 32 | 20·38 |
| $C^{12}NH^7S^2O^4$ | 157 | 100·00 |

Gerhardt regards this compound as the *nitride of sulphophenyl and hydrogen* $= N\left\{\begin{matrix} C^{12}H^5S^2O^4 \\ H \\ H \end{matrix}\right.$, in other words, as ammonia in which 1 At. H. is replaced by sulphophenyl, $C^{12}H^5S^2O^4$. By treating the com-

pound with various metallic salts, or with the chlorides of organic radicals, one or more of the remaining atoms of hydrogen may be replaced, *e. g.*

*Nitride of Sulphophenyl, Silver and Hydrogen*, $C^{12}NH^6AgS^2O^4$, or $N\left\{\begin{matrix}C^{12}H^5S^2O^4\\ H\\ Ag\end{matrix}\right.$, is obtained in the form of a white crystalline precipitate by treating an alcoholic and ammoniacal solution of sulphophenylamide with nitrate of silver.

*Nitride of Sulphophenyl, Sulphophenyl* and *Hydrogen*, or *Bisulphophenylamide*, $C^{24}NH^{11}S^4O^8 = N\left\{\begin{matrix}C^{12}H^5S^2O^4\\ C^{12}H^5S^2O^4\\ H\end{matrix}\right.$, is obtained in the crystalline form by gently heating the preceding silver-salt with chloride of sulphophenyl $C^{12}H^5S^2O^4,Cl$ [sulphite of chlorobenzene, (p. 174) ], treating the product with ether, which dissolves out the new compound, and leaving the ether to evaporate.

Similarly, by treating the sulphophenylamide with the chlorides of succinyl, $C^8H^4O^4Cl$, benzoyl $C^{14}H^5O^2Cl$, and cumyl $C^{20}H^{11}O^2Cl$, the compounds, $N\left\{\begin{matrix}C^{12}HS^2O^4\\ C^8\ H^4O^4\\ H\end{matrix}\right.$, &c. are obtained. From these nitrides containing 2 At. hydrogen replaced by organic radicals, silver-salts may be formed, such as $N\left\{\begin{matrix}C^{12}HS^2O^4\\ C^8\ H^4O^4\\ Ag\end{matrix}\right.$; and by treating such silver-salts with the chloride of an organic radical, a nitride may be formed containing three organic radicals, *e.g. nitride* of *sulphophenyl, benzoyl and cumyl*, $N\left\{\begin{matrix}C^{12}H^5S^2O^4\\ C^{14}H^5O^2\\ C^{20}H^{11}O^2.\end{matrix}\right.$ (Gerhardt, *Traité de Chimie organique*, III, 75.) ¶.

## ¶. *Amidogen-nucleus* $C^{12}Ad^2H^4$.

## Bithiobenzolic Acid.

$$C^{12}N^2H^6S^4O^{12} = C^{12}Ad^2H^4,4SO^3.$$

L. HILKENKAMP. *Ann. Pharm.* 95, 86.

*Dithiobenzolic acid, Phenyldisulphodiamic acid.*

*Formation.* By the action of sulphite of ammonia on binitrobenzene (pp. 203, 205).

The acid has not been obtained in the free state. All its salts are soluble in water; their general formula is $C^{12}N^2H^6M^2S^4O^{12}$ or $C^{12}Ad^2H^2M^2,4SO^3$: the acid is therefore bibasic.

*Bithiobenzolate of Ammonia.* — *Preparation* (*p.* 203). The needle-shaped crystals, after being pressed between paper, form a yellowish mass, which

when purified by washing with alcohol and ether, forms a perfectly white powder.

| | *Dried in vacuo.* | | | Kilkenkamp. |
|---|---|---|---|---|
| 12 C | 72 | .... | 23·84 | ........ 24·54 |
| 4 N | 56 | .... | 18·54 | ........ 18·20 |
| 14 H | 14 | .... | 4·64 | ........ 4·88 |
| 4 S | 64 | .... | 21·19 | ........ 21·21 |
| 12 O | 96 | .... | 31·79 | ........ 31·17 |
| $C^{12}N^2H^6(NH^4)^2,4SO^3$ | 302 | .... | 100·00 | ........ 100·00 |

The salt carbonises and intumesces when heated, giving off sulphurous acid. Sulphuric and hydrochloric acid, even when concentrated, do not act upon the salt in the cold; with the aid of heat, they eliminate a pungent gas, but no sulphurous acid. Nitric acid acts in the same manner, but likewise colours the cold solution yellow. Chlorine forms a considerable quantity of chloranil, together with traces of a brown resinous body. The salt dissolves very readily in water and aqueous alcohol, very sparingly soluble in absolute alcohol, and is insoluble in ether. The aqueous solution has an acid reaction.

*Bithiobenzolate of Baryta.* — Obtained by adding the ammonia-salt to boiling baryta-water, continuing the ebullition as long as ammonia goes off, removing the excess of baryta by carbonic acid, evaporating the filtrate till a crystalline substance begins to separate, and then leaving it to slow evaporation. It then yields crystalline crusts, which may be purified by filtering from the mother-liquor and washing with alcohol. The salt is white with a slight tinge of red, insoluble in alcohol anhydrous and hydrated, also in ether.

| | *Dried in vacuo.* | | | Hilkenkemp. |
|---|---|---|---|---|
| 12 C | 72·0 | .... | 17·85 | |
| 2 N | 28·0 | .... | 6·94 | |
| 6 H | 6·0 | .... | 1·49 | |
| 2 Ba | 137·2 | .... | 34·04 | ........ 33·73 |
| 4 S | 64·0 | .... | 15·87 | ........ 15·55 |
| 12 O | 96·0 | .... | 23·81 | |
| $C^{12}N^2H^6Ba^2,4SO^3$ | 403·2 | .... | 100·00 | |

¶. *Amidogen-nucleus* $C^{12}AdBr^2HO^2$.

## Bromanilamic Acid.

$C^{12}NBr^2H^3O^6 = C^{12}AdBr^2HO^2,O^4$.

STENHOUSE. *Phil. Mag. J.* [4], 8, 36; *Ann. Pharm.* 91, 313.

The red-brown solution of bromanil (p. 172), in strong aqueous ammonia, yields deep brown-red needles of a salt which appears to be bromanilamate of ammonia; and by cautiously adding sulphuric acid to the

aqueous solution of this salt, bromanilamic acid is separated in nearly black needles. If, on the other hand, the mixture is allowed to become heated, decolorisation takes place, and crystals separate having exactly the appearance of bromanilic acid (p. 171).

¶. *Amidogen-nucleus* $C^{12}Ad^2Br^2O^2$.

## Bromanilamide.

$$C^{12}N^2Br^2H^4O^4 = C^{12}Ad^2Br^2O^2,O^2.$$

STENHOUSE. *Phil. Mag. J.* [4], 8, 36; *Ann. Pharm.* 91, 312.

Obtained by passing dry ammoniacal gas into heated alcohol in which bromanil is suspended; also when bromanil is heated with alcohol and aqueous ammonia. The quantity of bromanilamide obtained by the latter method is however smaller, a larger portion of bromanilamate of ammonia, which is soluble in alcohol, being formed.

Brown-red, crystalline powder, which sublimes, with partial decomposition, in brown crystals. It is nearly insoluble in water, alcohol, and ether.

| | | | Stenhouse. |
|---|---|---|---|
| 12 C | 72 | 24·32 | |
| 2 N | 28 | 9·46 | |
| 2 Br | 160 | 54·06 | 54·21 |
| 4 H | 4 | 1·35 | |
| 4 O | 32 | 10·81 | |
| $C^{12}Ad^2Br^2H^2O^4$ | 296 | 100·00 | |

The specimen analysed was dissolved in alcohol containing a little potash, and precipitated by acetic acid. (Stenhouse.) ¶.

*Amidogen-nucleus* $C^{12}AdCl^2HO^2$.

## Chloranilamic Acid.

$$C^{12}NCl^2H^3O^6 = C^{12}AdCl^2HO^2,O^4.$$

ERDMANN. (1841.) *J. pr. Chem.* 22, 287.
LAURENT. *N. Ann. Chim. Phys.* 3, 493. *Rev. scient.* 19, 141; abstr. *J. pr. Chem.* 36, 280. *Compt. Chim.* 1845, 173.

*Chloranilamsäure, Chloranilam, Acide chloranilamique.*

The blood-red solution of chloranil in aqueous ammonia yields brown needles of chloranilammone: (chloranilamate of ammonia according to Laurent). (Erdmann, p. 198).

*Preparation.* 1. From the saturated aqueous solution of these needles, after addition of sulphuric or hydrochloric acid, the chloranilamic acid crystallises on cooling, in long black needles, which may be purified by pressure between paper, and crystallisation from the smallest possible quantity of boiling water.— Sometimes, especially when the addition of hydrochloric acid has produced too much heat, and the air has acted on the mixture, a brown powder mixes with the needles and must be removed by recrystallisation. The chloranilamic acid which remains dissolved in the acid mother-liquor of the needles, cannot be recovered by evaporation, which exerts a decomposing action, but may be obtained by extraction with ether and evaporation of the solvent. The mother-liquor of the chloranilammone yields a small extra quantity of chloranilamic acid, when treated with hydrochloric acid. — 2. The solution of chloranil in ammonia is supersaturated with hydrochloric acid, without previously separating the chloranilammone from the sal-ammoniac in the crystalline form, the mixture being constantly kept cool by cold water, and the crystals, which are scarcely contaminated with any brown powder, are purified by pressure between paper and recrystallisation from hot water. (Erdmann.)

The violet powder of the black needles gives up its water at 100°, and becomes lighter in colour. (Erdmann.)

| | *Anhydrous.* | | Erdmann. | Laurent. |
|---|---|---|---|---|
| 12 C | 72·0 | 34·65 | 35·08 | 34·0 |
| N | 14·0 | 6·73 | 7·40 | |
| 2 Cl | 70·8 | 34·07 | 33·24 | |
| 3 H | 3·0 | 1·45 | 1·75 | 1·5 |
| 6 O | 48·0 | 23·10 | 22·53 | |
| $C^{12}NCl^2H^3O^6$ | 207·8 | 100·00 | 100·00 | |

*Decompositions.* 1. The needles, when heated in a test tube, appear to sublime undecomposed to a slight extent, but afterwards give off yellow and brown, litmus-reddening vapours, and leave a residue of charcoal. — 2. The aqueous solution mixed with sulphuric or hydrochloric acid remains unaltered in the cold or at a gentle heat, even after a considerable time; but on being heated to the boiling point, the violet mixture, if the air is completely excluded, gradually becomes light red, the more quickly the stronger the acid added, and immediately or on cooling deposits crystals of chloranilic acid, whilst an ammonia-salt remains in solution :

$$C^{12}NCl^2H^3O^6 + 2HO = C^{12}Cl^2H^2O^8 + NH^3.$$

Strong acetic acid does not exert any decomposing action, even with half an hour's boiling. — The mixture of the acid with sulphuric or hydrochloric acid, boiled in contact with the air, *e.g.* in a basin, becomes covered on cooling with an iridescent film, and deposits a brown powder together with a few laminæ of chloranilamic acid. — 3. With aqueous potash, chloranilamic acid is resolved, even at 0°, into chloranilate of potash which crystallises, and ammonia which escapes. Also when heavy metallic salts are precipitated by chloranilamic acid or its ammonia-salt, more or less chloranilic acid appears to be produced, the salt of that acid forming at least a part of the precipitate. (Erdmann.)

*Combinations. Hydrated Chloranilamic acid.*— The above-mentioned black needles. They exhibit an adamantine lustre and yield a dark

violet powder. Between 100° and 130°, they give off 18·92 p.c. (somewhat more than 5 At.) water. They dissolve sparingly in water, forming a beautiful violet solution. (Erdmann.)

*Chloranilamate of Ammonia.* — *Chloranilammon.* (Erdmann.)— The deep blood-red solution of chloranil in warm aqueous ammonia yields, partly on cooling, partly after careful evaporation, small, shining, chestnut-coloured needles, which must be freed from the mother-liquor by draining on paper. (Erdmann.) These crystals are produced immediately on mixing ammonia with chloranilamic acid. (Laurent.)

| *Dehydrated at* 120°. | | | Erdmann. |
|---|---|---|---|
| 12 C | 72·0 | 32·03 | 33·06 |
| 2 N | 28·0 | 12·45 | 11·86 |
| 2 Cl | 70·8 | 31·49 | 31·62 |
| 6 H | 6·0 | 2·68 | 2·79 |
| 6 O | 48·0 | 21·35 | 20·67 |
| $C^{12}Cl^{2}Ad(NH^{4})O^{6}$ | 224·8 | 100·00 | 100·00 |

The crystals when dried give off 24·1 to 28 p.c. (therefore probably 8 At.) water. When heated in a test-tube, they yield a trace of violet sublimate, then a white sublimate, turning brown at the same time and becoming carbonised; heated on platinum-foil, they emit a purple smoke, and leave a difficultly combustible charcoal. The aqueous solution of the salt turns yellowish red when mixed with nitric acid, but does not deposit any thing. Mixed with sulphuric or hydrochloric acid, it assumes a violet colour in the cold, becoming deeper at a moderate heat, and deposits black needles of chloranilamic acid, while a portion of that acid remains in solution, together with sulphate or hydrochlorate of ammonia and a certain quantity of chloranilic acid, into which moreover, the whole of the chloranilamic acid is converted by boiling, a brown powder being also formed if the air has access to the liquid. (*vid. sup.*) Acetic acid does not decompose the salt. Cold potash slowly decomposes its aqueous solution, into chloranilate of potash which crystallises, and ammonia.— The salt dissolves in water, especially when hot, forming a purple solution. (Erdmann.)

The aqueous acid forms with *chloride of barium* a light brown precipitate, which dissolves with purple colour when the mixture is heated, but reappears on cooling in brown amorphous flakes, the liquid however retaining a reddish tint. (Erdmann.)

Aqueous chloranilamic acid, as well as the ammonia-salt, forms with neutral acetate *of lead*, a red-brown precipitate; with *ferric* and *nickel* salts, a blackish cloud; with *cupric* sulphate, after a while, and with the acetate immediately, a greenish brown precipitate; and with *mercurous* nitrate, a dark brown precipitate, whereas corrosive sublimate is not precipitated by it. (Erdmann.)

The thick red-brown precipitate formed with nitrate of *silver* (the liquid, even when the silver-solution is in excess, retaining a deep violet colour, and depositing red-brown, often crystalline flakes when evaporated,) is decomposed by nitric acid, with formation of chloride of silver, and dissolves completely in hot water, as well as in ammonia and acetic acid. (Erdmann.)

The silver-salt varies in composition according to the mode of preparation: *a*. Precipitated cold; *b*. Precipitated warm; *c*. The crystalline flakes deposited from the liquid filtered warm from *b*. The preparations were dried in each case at 130°. (Erdmann.) [Laurent appears to have precipitated his salt in the cold. It is probable that generally a mixture of chloranilate and chloranilamate of silver is produced, but that the latter is more soluble in warm water, and is, therefore, for the most part, precipitated from warm mixtures on cooling in the form *c*.] Erdmann takes another view.

| | | | *a.* | *b.* | *c.* | Laurent. |
|---|---|---|---|---|---|---|
| 12 C | 72·0 | 22·87 | 21·50 | | | 21·80 |
| N | 14·0 | 4·44 | | | | 4·80 |
| 2 Cl | 70·8 | 22·49 | 20·70 | 17·90 | 21·1 | |
| 2 H | 2·0 | 0·64 | 0·57 | | | 0·62 |
| Ag | 108·0 | 34·31 | 40·40 | 43·58 | 34·17 | |
| 6 O | 48·0 | 15·25 | | | | |
| $C^{12}Cl^2AdAgO^6$ | 314·8 | 100·00 | | | | |

*Amidogen-nucleus* $C^{12}Ad^2Cl^2O^2$.

## Chloranilamide.

$$C^{12}N^2Cl^2H^4O^4 = C^{12}Ad^2Cl^2O^2.$$

LAURENT. (1845.) *Rev. scient.* 19, 141; abstr. *J. pr. Chem.* 36, 283.

*Formation.* (p. 198.)

*Preparation.* Chloranil dissolved in alcohol is gently heated with ammonia; the resulting dark red-brown precipitate freed from the alcoholic liquid, washed with alcohol, dissolved in gently heated alcohol containing potash, care being taken not to heat too long or too strongly; the solution, filtered if necessary, neutralised while yet warm with acetic acid; and the quickly formed brown-red crystalline precipitate, collected on a filter, washed and dried.

*Properties.* Dark carmine-coloured powder, consisting of fine needles and having an almost metallic lustre. When carefully heated on a glass plate, it sublimes almost entirely in crystalline tufts, resting on a layer of charcoal.

| | | | Laurent. |
|---|---|---|---|
| 12 C | 72·0 | 34·82 | 35·2 |
| 2 N | 28·0 | 13·54 | 13·4 |
| 2 Cl | 70·8 | 34·24 | 34·0 |
| 4 H | 4·0 | 1·93 | 1·9 |
| 4 O | 32·0 | 15·47 | 15·5 |
| $C^{12}N^2Cl^2H^4O^4$ | 206·8 | 100·00 | 100·0 |

*Decompositions.* Chloranilamide boiled with potash-ley, is resolved into ammonia, which escapes, and chloranilate of potash which crystallises:

$$C^{12}N^2Cl^2H^4O^4 + 2KO + 2HO = C^{12}Cl^2K^2O^8 + 2NH^3.$$

It is not decomposed by boiling with aqueous or alcoholic hydrochloric acid.

*Combinations.* It dissolves in *water* and in aqueous *ammonia*.

Its violet-red solution in oil of vitriol is coloured blue by a small quantity of water and wine-red by a larger quantity; and when treated with a still larger quantity, deposits a portion of the chloranilamide, provided the quantity of water and acid present is not too great.

From its solution in *alcoholic potash*, it is precipitated unaltered by acids.

It is nearly insoluble in *alcohol* and *ether*. (Laurent.)

### ¶. *Amidogen-nucleus* $C^{12}X^2AdH^3$.

## Picramic Acid.

$$C^{12}N^3H^5O^{10} = C^{12}X^2AdH^3,O^2.$$

WÖHLER. *Pogg.* 13, 488.
A. GIRARD. *Compt. rend.* 36, 421; *J. pr. Chem.* 59, 142. *Ann. Pharm.* 88, 281; — further: *Compt. rend.* 42, 59; *J. pr. Chem.* 67, 507.
E. PUGH. *Ann. Pharm.* 96, 83; *J. pr. Chem.* 65, 362.

*Nitrohæmatic acid, Deoxidised Picric acid.*

*Formation and Preparation.* (pp. 218, 219.) Girard's method by the action of sulphuretted hydrogen appears to be the most productive.

*Properties.* The acid separated from its ammonia-salt by acetic acid forms beautiful red needles, often grouped in tabular masses. (Girard); from an ethereal solution, it crystallises in distinct prismatic crystals with very acute terminal faces, garnet-coloured by reflected, yellowish-red by transmitted light. (Pugh.) Has a slightly bitter taste (Girard); does not taste bitter. (Pugh.) Melts at 165°, and solidifies in a crystalline mass on cooling. (Girard.)

| | *Crystals.* | | Girard (*mean*). |
|---|---|---|---|
| 12 C | 72 | 36·1 | 35·6 |
| 3 N | 42 | 21·1 | 21·4 |
| 5 H | 5 | 2·5 | 2·8 |
| 10 O | 80 | 40·3 | 40·2 |
| $C^{12}X^3AdH^3,O^2$ | 199 | 100·0 | 100·0 |

*Decompositions.* 1. The acid heated above 165° is decomposed, with evolution of tarry vapours containing hydrocyanic acid and ammonia, and leaves a residue of charcoal. (Girard, Wöhler, p. 218.) It burns vividly when thrown on red-hot coals. (Girard.) — 2. It dissolves at ordinary temperatures in sulphuric acid, forming a red solution, from which, on dilution with water and addition of ammonia, the picramic acid separates out unaltered: similarly with hydrochloric acid; but by hot

concentrated sulphuric acid it is decomposed and carbonised. (Girard.) 3. Strong nitric acid decomposes it, with abundant evolution of nitrous fumes, the liquid assuming a straw-yellow colour and the picramic acid being converted into picric acid. (Girard, Pugh.) According to Wöhler, nitrohæmatic acid is not reconverted into picric acid by the action of nitric acid (p. 218).

*Combinations.* The acid dissolves with some difficulty in *water*, forming a yellow solution. (Wöhler.) It is nearly insoluble in water even at the boiling heat. (Girard.)

Picramic acid unites readily with *bases.* Its salts are mostly crystalline; their general formula is $C^{12}X^2AdH^2M, O^2$.

*Picramate of Ammonia.* — *Preparation* (*p.* 219).—Separates from the alcoholic solution by spontaneous evaporation, in dark orange-red rhombohedral tables. Does not decompose at 100°, but at 135° it effloresces and gives off ammonia; melts at 165°, and decomposes at a higher temperature. It dissolves readily in water and alcohol, forming deep red solutions, but is insoluble in ether. The aqueous solution is decomposed by continued boiling, with separation of a brown powder. (Girard.)

| | | | Girard. |
|---|---|---|---|
| 12 C | 72 | 33·33 | |
| 4 N | 56 | 25·93 | 26·9 |
| 8 H | 8 | 3·70 | |
| 10 O | 80 | 37·04 | |
| $C^{12}X^2AdH^2(NH^4),O^2$. | 216 | 100·00 | |

*Picramate of Potash.* — Obtained by decomposing the hot solution of the ammonia-salt with potash. Separates on cooling in red transparent elongated rhombic tables, containing 19·9 p. c. potash. Decomposes with slight detonation when somewhat strongly heated, and leaves a residue of charcoal. Dissolves pretty easily in water, sparingly in alcohol. (Girard.)

| | | | Girard. |
|---|---|---|---|
| KO | 47·2 | 19·8 | 19·9 |
| $C^{12}N^3H^4O^9$ | 190·0 | 80·2 | |
| $C^{12}X^2AdH^2K,O^2$ | 237·2 | 100·0 | |

*Picramate of Baryta.* — On decomposing a hot solution of picramate of ammonia with nitrate of baryta, this salt separates in small silky tufts of red and golden-yellow needles. It bears a heat of 200° without decomposition, but detonates at a higher temperature, leaving a residue of charcoal. Dissolves sparingly in water and alcohol. Contains 27·9 p. c. baryta. (Girard.)

| | | | Girard. |
|---|---|---|---|
| BaO | 76·6 | 27·8 | 27·9 |
| $C^{12}N^3H^4O^9$ | 190·0 | 72·2 | |
| $C^{12}X^2AdH^2Ba,O^2$ | 266·6 | 100·0 | |

The soluble picramates give no precipitate with salts of *manganese.* (Girard.)

*Picramate of Lead.* — Orange-coloured powder which explodes when heated, and also by percussion, but without much noise. Dissolves in water, ammonia and acids, but is insoluble in alcohol. (Girard.)

Soluble picramates do not precipitate the salts of *iron, cobalt,* or *nickel.*

*Picramate of Copper.* — Yellowish green, amorphous precipitate, which detonates slightly, is insoluble in water and alcohol, but soluble in acids. (Girard.)

| | | | Girard. |
|---|---|---|---|
| CuO | 40 | 17·3 | 17·2 |
| $C^{12}N^3H^4O^9$ | 190 | 82·7 | |
| $C^{12}X^2AdH^2Cu,O^2$ | 230 | 100·0 | |

With *mercuric salts,* the soluble picramates form a red precipitate soluble in acids.

*Picramate of Silver.*—Obtained by decomposing the ammonia-salt with nitrate of silver, in the form of a brick-red amorphous precipitate, which does not blacken by exposure to light, but decomposes, with blackening, at about 140°, leaving a residue which melts at about 165°. On glowing coals, it burns without detonation. It is insoluble in cold water and in alcohol. Boiling water decomposes it, leaving an insoluble residue. (Girard.)

| | | | Girard. | Pugh. |
|---|---|---|---|---|
| AgO | 116 | 37·9 | 37·3 | 37·75 |
| $C^{12}N^3H^4O^9$ | 190 | 62·1 | | |
| $C^{12}X^2AdH^2Ag,O^2$ | 306 | 100·0 | | |

¶. *Amidogen-nucleus* = $C^{12}X^3AdH^2$.

## Picramide.

$C^{12}N^4H^4O^{12} = C^{12}X^3AdH^2$.

PISANI. *Compt. rend.* 39, 852; *Ann. Pharm.* 92, 326.

Obtained by the action of ammonia on chloropicryl (p. 236). When crude chloropicryl (containing oxychloride of phosphorus) is triturated in the cold with excess of carbonate of ammonia, and the mass treated with boiling water, a residue is obtained consisting of picramide, which dissolves in boiling alcohol, and separates in crystalline plates, dark yellow by transmitted, violet by reflected light: its powder is light yellow. When heated, it decomposes without detonation, giving off nitrous fumes, and leaving a carbonaceous residue. Heated with aqueous potash, it gives off ammonia and yields picrate of potash:

$$[C^{12}X^3(NH^2)H^2 + KO,HO = C^{12}X^3H^2K,O^2 + NH^3].$$

Dissolves sparingly in ether. (Pisani.) ¶.

*Nitrogen or Azo-nucleus* $C^{12}NH^5$.

## Aniline.

$$C^{12}NH^7 = C^{12}NH^5,H^2.$$

UNVERDORBEN. (1826.) *Pogg.* 8, 397.
RUNGE. *Pogg.* 31, 65 and 513; 32, 331.
FRITZSCHE. *J. pr. Chem.* 30, 453; 27, 153; 28, 202.
ZININ. *J. pr. Chem.* 27, 149; 36, 98.
A. W. HOFMANN. *Ann. Pharm.* 47, 31; 53, 8; 57, 265; 66, 129; 67, 61 and 129; 70, 129; 74, 117; 75, 356.
HOFMANN & MUSPRATT. *Ann. Pharm.* 53, 221; 57, 210.
LAURENT. *Compt. rend.* 17, 1366; also *J. pr. Chem.* 32, 286. — *Rev. scientif.* 18, 278 and 280; also *J. pr. Chem.* 36, 13.
GERHARDT. *N. J. Pharm.* 9, 401; also *N. Ann. Chim. Phys.* 14, 117. — *N. J. Pharm.* 10, 5.
LAURENT & GERHARDT. *N. Ann. Chim. Phys.* 24, 163; also *N. J. Pharm.* 14, 130; also *Ann. Pharm.* 68, 15.

*Krystallin* (Unverdorben), *Kyanol* (Runge), *Anilin* (Fritzsche), *Benzidam* (Zinin), *Phänamid, Phenylamine* (Hofmann), *Amidophénase.*

*Formation.* 1. By heating carbolate of ammonia for some time by itself in a sealed tube:

$$NH^3,C^{12}H^6O^2 = C^{12}NH^7 + 2HO.$$

At 200°, only a trace of aniline is formed in half-an-hour; but between 200° and 300°, a large quantity in the course of 18 days. (Laurent.) — 2. When nitrobenzene is decomposed by sulphuretted hydrogen in presence of alcohol and ammonia (Zinin, p. 672), or by zinc in presence of alcohol and hydrochloric acid (Hofmann, p. 672), or by ferrous acetate;

$$C^{12}NH^5O^4 + 12FeO + 2HO = 6Fe^2O^3 + C^{12}NH^7.$$

Ferrous sulphate, oxalate and chloride, do not exert any action upon nitrobenzene. (A. Béchamp, *N. Ann. Chim. Phys.* 42, 186.) — 3. By distillation of azoxybenzene. (Zinin.) — 4. By distillation of anthranilic acid. (Fritzsche.) — 5. By passing the vapour of salicylamide, or nitrotoluene, which is isomeric with it, over lime at a low red heat. (Hofmann and Muspratt.) Nitrometastyrol yields but a small quantity. (Hofmann & Blyth.) — 6. By distilling indigo *per se* (Unverdorben), or with very strong potash-ley. (Fritzche.) — 7. In the dry distillation of coal, aniline passes over with the coal-tar. (Runge.) In the tar obtained by the distillation of animal substances, Hofmann did not find aniline; Anderson, however, found it in the product of the distillation of bones.

*Preparation.* 1. From *Nitrobenzene.* — *a.* Nitrobenzene dissolved in alcohol is mixed with ammonia; sulphuretted hydrogen passed through the solution; the greater part of the alcohol gradually distilled, after a few days, from the liquid which contains crystals of sulphur, the liquid being cooled and decanted from the gradually deposited sulphur as often

as it causes percussive ebullition; and the distillation continued, after all the sulphur has separated, as long as the contents of the retort continue to deposit aniline in the form of a yellow oil at the bottom of the slightly alcoholic liquid: the oil thus deposited is afterwards rectified *per se.* (Zinin.) — *b.* Nitrobenzene dissolved in alcohol and distilled with an equal weight of hydrate of potash, is converted into azoxybenzene, which, by further distillation, is resolved into aniline, which passes over first and remains liquid, and azobenzene which passes over later and crystallises. The more volatile aniline is freed from the greater part of the azobenzene by fractional distillation, and dissolved in boiling dilute sulphuric acid; and the resulting solution, decanted from the azobenzene, which sinks to the bottom in the form of an oil, yields, on cooling, crystals of sulphate of aniline, which, when purified by recrystallisation and distilled with potash-ley, yield pure aniline. (Zinin.) ¶. *c.* Nitrobenzene and ferrous acetate (3 pts. iron to 1 pt. nitrobenzene) are mixed in a flask fitted with a distillation-tube to condense any acetate of aniline that may pass over, and heated in the water-bath; the contents of the flask then filtered (after being stirred up with water if too pasty); the residue on the filter washed with hot water; and the entire liquid distilled: acetate of aniline and free acetic acid then pass over together with the watery vapours. The distillate is mixed with strong sulphuric acid (4 pts. acid to 10 pts. of nitrobenzene used) and the mixture distilled to expel the acetic acid; sulphate of aniline then remains and may be purified by recrystallisation from alcohol, or immediately distilled with potash to separate the aniline. — When 1 pt. of nitrobenzene, $1\frac{1}{2}$ pts. of pure iron-filings, and 1 pt. of strong acetic acid, are introduced into a retort, a brisk action soon begins without external heating:

$$C^{12}NH^5O^4 + 4Fe + 2HO = 2Fe^2O^3 + C^{12}NH^7;$$

and aniline, acetate of aniline, and a small quantity of undecomposed nitrobenzene collect in the receiver, which must be well cooled. The contents of the receiver are then poured back into the retort and distilled to dryness, and aqueous aniline separated from the distillate by caustic potash. (A. Béchamp, *N. Ann. Chim. Phys.* 42, 186.) ¶.

2. *From Indigo.* — *a.* The oil obtained by the dry distillation of indigo is extracted by an acid. (Unverdorben.) — *b.* Indigo-powder is introduced into highly concentrated potash-ley heated in a retort; the resulting brown mass heated as long as ammoniacal water and a brown oil pass over with strong intumescence; and the oil separated by distillation into a brown resinous residue, and a colourless distillate of aniline, amounting to 20 per cent. of the indigo. (Fritzsche.)

3. *From Coal-tar.* — *a.* The tar is distilled till pitch remains behind; the pitch distilled with a quantity of sulphuric acid sufficient to retain the greater part of the ammonia, the receiver being changed as soon as the distillate sinks in water; the oil which sinks in water, the *heavy oil* (the first portions of which contain a considerable quantity of aniline with but little leucol, while the subsequent portions consist chiefly of leucol), violently shaken in a carboy with strong commercial hydrochloric acid; this acid, after 24 hours' standing, separated by the siphon from exhausted oil floating on the surface, in order that it may be repeatedly treated with fresh oil, which may amount to 100 lbs. in all, and may take up a large quantity of bases; and the acid liquid strained through cloth or grey paper, mixed with milk of lime in a copper-still which must be immediately closed, and distilled over a strong fire, with good arrange-

ments for cooling. It then yields a first distillate consisting of a milky liquid having an intoxicating odour, and with brown-black oily drops floating on its surface; and afterwards, when about half has passed over, and the odour of the distillate has become more agreeable and somewhat like that of bitter almonds, a second distillate, to be collected in a separate receiver, and consisting of a turbid watery liquid which holds but little oil in solution. The first distillate becomes clear when mixed with hydrochloric acid, and if mixed with potash after evaporation, deposits drops of an oil having an intoxicating odour, and consisting mainly of aniline and leucol, but containing also a small quantity of neutral oil. This oil does not dissolve completely in hydrochloric acid: hence, after removing the watery liquid, it must be dissolved in ether; shaken up with hydrochloric or sulphuric acid; and the liquid carefully separated from the ether, in which the neutral oil remains dissolved, and mixed in a tall cylindrical vessel with hydrate of potash or strong potash-ley, by which the basic oil is generally separated in the form of a layer which rises to the surface and may be removed with the pipette. If it should separate merely in fine drops which fill the entire liquid, they must be made to unite and rise to the surface, by mixing the liquid with common salt and setting it aside for several days, and, if this method does not succeed, saturating the water with hydrate of potash; or else: the mixture may be distilled with water, whereupon the oil, amounting to $\frac{1}{250}$ of the heavy coal-tar oil, collects in drops on the surface of the distillate.—*a*. The oily mixture of aniline and leucol thus obtained is distilled (to about $\frac{4}{5}$) till a drop which passes over no longer turns blue with solution of chloride of lime; and the dark yellow distillate having an intoxicating odour, dehydrated by setting it aside for some days in contact with an equal quantity of hydrate of potash, then separated from the potash-solution by the pipette, and rapidly distilled in a current of dry hydrogen, setting aside the first fourth which may contain water, and the last pale yellow portion which contains leucol. On redistilling the middle half, which is colourless, and again collecting apart the middle half of the distillate, aniline is obtained nearly pure, but still contaminated with a very small quantity of a substance which has a penetrating offensive odour (Anderson's picoline), and makes it lighter than water. But by combining it with oxalic acid, purifying the oxalate of aniline by repeated crystallisation from alcohol, and distilling with potash, this odour may be entirely removed.—*β*. Or, the mixture of aniline and leucol is dissolved in absolute alcohol, neutralised with alcoholic oxalic acid, and the mother-liquor, which contains scarcely anything but oxalate of leucol, decanted, after standing for some hours, from the oxalate of aniline which separates in the form of a white crystalline mass. (Hofmann.)

*b*. The oil obtained by distilling coal-tar over oxide of copper, is set aside for 8 hours with $\frac{1}{6}$ pt. lime and 4 pts. water, the mixture being frequently shaken; the brownish yellow watery liquid filtered and distilled to one-half; the distillate (consisting of a thick oil and a watery liquid, and containing carbolic acid, ammonia, aniline, leucol and pyrrhol) mixed with excess of hydrochloric acid, distilled to remove the carbolic acid and pyrrhol, till the liquid which passes over is no longer coloured red, but yellow, by nitric acid; the dark yellow residue distilled with excess of soda-ley; the distillate consisting of ammonia, aniline, and leucol, distilled with excess of acetic acid, as long as the liquid which passes over colours fir-wood yellow, the greater part of the acetate of ammonia then remaining in the retort; part of the distillate, consisting of acetate

of aniline and leucol, and a small quantity of acetate of ammonia, distilled with oxalic acid, whereupon the acetic acid passes over; then, in order to saturate the oxalic acid with bases, a second portion, &c. &c. till the liquid which passes over colours fir-wood yellow, and therefore contains acetate of aniline (which, together with the acetate of leucol, must be collected in a separate receiver), a proof that the oxalic acid is saturated. The residue in the retort, consisting of oxalate of aniline and leucol, a small quantity of oxalate of ammonia, and a brown-red colouring matter, is evaporated to dryness, and washed on a filter with 85 per cent. alcohol, as long as anything dissolves, collecting apart the last and slightly coloured portion of alcohol which runs through. That which remains on the filter is oxalate of aniline; the slightly coloured alcoholic filtrate contains the oxalates of aniline and leucol, which crystallise on evaporation, and may be so far separated by recrystallisation from hot water (on the cooling of which the leucol-salt crystallises first in colourless needles, and then the aniline-salt in laminæ), and from alcohol, that the aniline-salt, when rubbed between the fingers, no longer smells like phosphorus, and the leucol-salt neither colours fir-wood yellow nor chloride of lime violet. By distilling the oxalates with soda-ley, agitating the distillate with ether, and evaporating the ethereal extracts, the bases are obtained in the free state. (Runge.)

*Properties.* Thin colourless oil (Runge), becoming thickish at — 20° but not solidifying (Hofmann): sp. gr. 1·028 (Fritzsche); 1·020 at 16° (Hofmann); refracts light very strongly (Fritzsche, Hofmann); does not at all conduct the current of a 4-celled Bunsen's battery. (Hofmann.) Boils steadily at 182° (Hofmann), at 228° (Fritzsche); at about 200° (Zinin), and soon evaporates when exposed to the air (Runge), so that an oil-stain produced on paper by aniline, soon disappears. (Hofmann.) Vapour-density = 3·219 (Burral, *N. Ann. Chim. Phys.* 20, 348.) Smells strongly like fresh honey (Unverdorben); has a very faint, not unpleasant odour, and when inhaled does not act injuriously on the head or lungs (Runge); has a strong, unpleasant, aromatic odour (Fritzsche); a peculiar odour (Zinin); a faint, agreeable, vinous odour. (Hofmann.) Its taste is somewhat biting (Zinin); aromatic and burning. (Hofmann.) Half a gramme of aniline introduced, together with $1\frac{1}{2}$ grm. water, into the stomach of a rabbit, causes strong clonic cramps, then laborious breathing, loss of strength, dilated pupils, and inflammation of the mucous membrane of the mouth; but aniline dropt into the eye does not dilate the pupil. (Hofmann.) It does not exert any poisonous action on dogs (Wöhler & Frerichs, *Ann. Pharm.* 65, 343); its aqueous solution kills leeches, and cut pieces of plants immersed in it. (Runge.) — Aniline does not blue reddened litmus (Runge), or redden turmeric (Runge); neither does its aqueous solution, which however turns the violet colour of dahlias to green. (Hofmann.) It imparts a bright violet-blue colour to chloride of lime; and in presence of an acid, a yellow colour to firwood and elder-pith. (Runge.)

| | | | Zinin. *from Nitrobenzene.* | Zinin. *from Azoxibenzene.* | Fritsche. *from Indigo.* | Hofmann. *from Coal-tar.* |
|---|---|---|---|---|---|---|
| 12 C | 72 | 77·42 | 77·17 | 77·11 | 78·21 | 77·31 |
| N | 14 | 15·05 | 14·84 | 15·00 | 14·83 | |
| 7 H | 7 | 7·53 | 7·61 | 7·51 | 7·54 | 7·72 |
| $C^{12}NH^7$ | 93 | 100·00 | 99·62 | 99·62 | 100·58 | |

| | Vol. | | Density. |
|---|---|---|---|
| C-vapour .......... | 12 | .............. | 4·9920 |
| N-gas.................. | 1 | .............. | 0·9706 |
| H-gas .............. | 7 | .............. | 0·4851 |
| Aniline-vapour .... | 2 | .............. | 6·4477 |
| | 1 | .............. | 3·2236 |

According to Laurent and most chemists, aniline is $C^{12}AdH^5$ and not $C^{12}NH^5,H^2$. According to Hofmann it is *phenylamine* $N\begin{cases}C^{12}H^5\\H\\H\end{cases}$, that is, ammonia in which 1 At. H is replaced by phenyl.

*Decompositions.* 1. Aniline *burns* when set on fire, with a luminous, strongly fuliginous flame. (Hofmann.) — 2. When exposed to the *air*, it becomes yellow (red, according to Zinin), and afterwards brown, forming a resin, which is brown according to Fritzsche, red, and soluble with yellow colour in water, according to Unverdorben; the change takes place the more quickly as the temperature is higher. (Hofmann.) Hence in distilling aniline, it is necessary, either to use a brisk fire, or to pass a stream of carbonic acid or hydrogen gas through the apparatus. (Hofmann.)

3. *Chlorine gas* passed through dry aniline, converts it, with great rise of temperature and evolution of hydrochloric acid, into a black viscid tar, which stops up the gas-delivery tube. If, in order to prevent this accident, the chlorine be passed through aniline mixed with water, or dissolved in hydrochloric acid or in alcohol, the liquid, which assumes first a blue, then a black colour, deposits a black tar, which on cooling solidifies into a brittle resin;—and this resin distilled with a small quantity of water, yields terchloraniline, $C^{12}NCl^3H^4$; afterwards liquefies; leaves a residue of charcoal; and gives off hydrochloric acid and terchlorocarbolic acid in the form of a yellow offensive oil which crystallises on cooling. (Hofmann.):

$$C^{12}NH^7 + 6Cl = \underbrace{C^{12}NCl^3H^4}_{\text{terchloraniline.}} + 3HCl;$$

and :

$$C^{12}NH^7 + 6Cl + 2HO = \underbrace{C^{12}Cl^3H^3O^2}_{\text{terchlorocarbolic acid.}} + 2Cl + NH^4Cl.$$

Terchloraniline appears also to be formed when aniline is distilled with hydrochloric acid and peroxide of manganese. (Hofmann.)

4. Bromine forms with anhydrous aniline, with great evolution of heat, a brown solution, which, if the quantity of bromine is sufficient, solidifies to a mixture of finely crystalline terbromaniline and hydrobromic acid. (Fritzsche.) — *Bromine water* added to aniline dissolved in hydrochloric acid, forms a considerable quantity of hydrobromic acid, and a precipitate of terbromaniline which quickly becomes crystalline; the same substance is deposited, after boiling aniline with excess of hydrobromic acid, in the form of a dark-coloured oil which crystallises on cooling. (Hofman.) — 5. The dark brown solution of *iodine* in aniline, the formation of which is attended with great rise of temperature, soon deposits long needles of hydriodate of aniline (Fritzsche, Hofmann), while the mother-liquor retains, together with a portion of this salt and

iodine (free, and capable of extraction by potash), an ioduretted, brown, amorphous resin, insoluble in water, acids and alkalis, but soluble in alcohol and ether, and likewise hydriodate of iodaniline: formation of the last-mentioned compound:

$$C^{12}NH^7 + 2I = C^{12}NIH^6,HI. \quad \text{(Hofmann.)}$$

6. With aqueous *chloride of lime,* aniline forms an azure or violet-blue solution, which is coloured rose-red by acids and decolorised by a large quantity of chlorine, in consequence of the formation of an acid [?] which forms blue salts with bases, as in this case with lime. Hence coal-tar shaken up with dilute chloride of lime, forms a blue watery liquid. (Runge.) All hypochlorites act like chloride of lime. The blue mixture becomes covered in a few minutes with an iridescent film, and gradually assumes a dingy red colour (more quickly with aniline-salts). The alcoholic solution of aniline acquires but a faint blue colour when mixed with chloride of lime; the ethereal solution, or a solution containing a large quantity of ammonia is not coloured at all. (Hofmann.)—7. On adding to the aqueous solution of an aniline-salt, an equal quantity of alcohol, and then *hydrochloric acid* mixed with *chlorate of potash,* a considerable quantity of indigo-coloured flakes is gradually deposited; and these, when collected on a filter and washed with alcohol, become green as they are freed from adhering acid, and shrink in drying, into a dark green body containing 16 per cent of chlorine. The liquid filtered from the blue precipitate contains a brown resin, and when boiled, with addition of more hydrochloric acid and chlorate of potash, assumes a light yellow colour and yields crystals of chloranil. Bromic acid or a mixture of iodate of potash and sulphuric acid, forms with aniline a similar blue precipitate. (Fritzsche.) As the proportion of hydrochloric acid and chlorate of potash required to form the blue precipitate is not easily found, it is better to add to a solution of aniline in hydrochloric acid, a few drops of chlorous acid prepared by Millon's process, which immediately forms a blue magma. The washed precipitate is decomposible by ammonia or potash, with formation of sal-ammoniac or chloride of potassium. By gradually adding chlorate of potash to a boiling mixture of strong hydrochloric acid and aniline dissolved in a not too large quantity of alcohol, crystals of pure chloranil are obtained, without any blueing of the mixture, but with copious evolution of acetic ether and formation of sal-ammoniac. When a large quantity of chlorate of potash is thrown into a boiling solution of aniline in excess of strong hydrochloric acid, a brisk reaction takes place, and chloranil is produced, together with a red resin which may be extracted by alcohol, and when distilled, yields, first an additional quantity of chloranil, then hydrochloric acid, and afterwards a sublimate having the odour and chemical relations of terchlorocarbolic acid, but probably consisting of quintichlorocarbolic acid. (Hofmann.) — 8. Aniline is decomposed by *nitric acid,* and when evaporated at 100°, leaves a brown-black residue. (Runge.) — It is immediately reddened by strong nitric acid. (Zinin.) It acquires a transient blue and green colour by treatment with strong nitric acid. (Fritzche.) — With a small quantity of fuming nitric acid, it immediately forms a deep azure-blue mixture, which when very slightly warmed, turns yellow, becomes hot, gives off gas with violence, then assumes a scarlet colour continually increasing in brightness, and deposits numerous plates of picric acid. (Hofmann.) Aniline, dissolved in moderately strong nitric acid, likewise passes into spontaneous ebullition on the application of a

gentle heat, gives off nitrous vapours, and when that action ceases, is found to be converted into picric acid, (Hofmann & Muspratt):

$$C^{12}NH^7 + 6NO^5 = C^{12}N^3H^3O^{14} + 4HO + 4NO^3. \quad \text{(Hofmann.)}$$

9. Aqueous hydrochlorate of aniline mixed with *nitrate of silver* (or with nitre which has been heated to redness for some time) gives off a large quantity of nitrogen gas, and yields carbolic acid in small brown oily drops. (Hunt, *Sill. Am. J.*, 1849; Hofmann, *Ann. Pharm.* 75, 356):

$$C^{12}NH^7 + NO^3 = C^{12}H^6O^2 + HO + 2N. \quad \text{(Hunt.)}$$

Hunt produced the same transformation by passing nitric oxide gas through a solution of aniline in nitric acid, whereas Hofmann, by using comparatively strong acid, obtained a brown resinous mixture of crystalline nitrocarbolic acid, and an amorphous substance, together with a trace of carbolic acid, to judge by the odour of castoreum which was evolved; with a weaker acid, no decomposition took place. — 10. *Oil of Vitriol* forms with aniline a mixture which turns brown at 100°, and when the decomposition is carried further, produces sulphate of ammonia. (Runge.)

11. Aniline takes fire, in contact with anhydrous *chromic acid*, and burns with a bright flame and agreeable odour, leaving sesquioxide of chromium. (Hofmann.) — The aqueous solution of aniline and its salts, forms with aqueous chromic acid, a precipitate containing chromium, which is dark blue, dark green, or black, according to the concentration of the solutions (Fritzsche, Hofmann), and varies in composition from 62·66 p.c. C and 2·12 $Cr^2O^3$ to 33·93 C and 31·00 $Cr^2O^3$. (Fritzsche.) — 12. Aniline and its salts form in solution of *permanganate of potash*, a brown precipitate of hydrated peroxide of manganese. (Fritzsche, Hofmann.) — 13. When aqueous sulphate of aniline is boiled with *peroxide of lead*, carbolic acid is evolved, and a blue liquid produced, which smells of formic acid, afterwards becomes colourless, and gives off ammonia when treated with potash. (Hofmann.) — 14. With *ferric sulphate*, sulphate of aniline forms a dark red mixture from which ferrous sulphate crystallises. (Hofmann.) — 15. Aniline heated with *solution of silver*, forms a black brown precipitate, and with *solution of gold*, a purple flocculent precipitate. (Runge.)

16. With *terchloride of phosphorus*, aniline forms a crystalline substance. (Hofmann.) — 17. In *phosgene gas* it becomes heated and solidifies into a crystalline mixture of carbanilide and hydrochlorate of aniline:

$$4C^{12}NH^7 + 2CClO = C^{26}N^2H^{12}O^2 + 2(C^{12}NH^7,HCl). \quad \text{(Hofmann.)}$$

18. Aniline mixes in all proportions with *bisulphide of carbon*, the mixture giving off sulphuretted hydrogen, after standing for several hours, and solidifying after some weeks (more quickly in a warm place or on addition of alcohol), forming scaly sulphocarbanilide:

$$2C^{12}NH^7 + 2CS^2 = C^{26}N^2H^{12}S^2 + 2HS \text{ (Hofmann).}$$

20. Aniline mixed with *iodide of methyl*, boils briskly and forms crystals of hydriodate of methylaniline:

$$C^{12}NH^7 + C^2H^3I = C^{14}NH^9,HI.$$

Similarly with *bromide of methyl*, it quickly solidifies into a mass of hydrobromate of methylaniline. (Hofmann.)—21. *Cyanogen gas* passed through pure aniline is quickly absorbed, with evolution of heat, and a reddening of the liquid amounting to opacity; an odour of hydrocyanic

acid is at the same time produced, which, when the passage of the gas is continued, changes into that of cyanogen, but after the vessel has been closed for 12 hours, again passes into that of hydrocyanic acid; the liquid deposits crystalline but brown cyaniline, and, if sufficient cyanogen is present, finally solidifies into a dark crystalline mass. When cyanogen is passed through an alcoholic solution of aniline, only till the liquid smells strongly of it, crystals of nearly pure cyaniline are deposited; but when the passage of the gas is further continued, other products mix with the cyaniline, just as when the gas is passed through pure aniline. (Hofmann.) — 22. Anhydrous aniline absorbs the vapour of *cyanic acid* evolved from heated cyanuric acid, becoming hot, and solidifying as it cools, in the form of crystalline aniline-urea, $C^{14}N^2H^8O^2$, mixed with a quantity of carbanilide, $C^{26}N^2H^{12}O^2$, greater, as the liquid has become more strongly heated:

$$C^{12}NH^7 + C^2NHO^2 = C^{14}N^2H^8O^2.$$

The same aniline-urea is precipitated in the crystalline form on adding *cyanate* of potash to aqueous sulphate of aniline. (Hofmann, *Ann. Pharm.* 53, 57; 57, 365.) Chancel (*Compt. chim.* 1849) obtained by the latter process nothing but cyanate of aniline, which gave off all the aniline on being boiled with potash. — 23. *Gaseous chloride of cyanogen* dried by chloride of calcium is absorbed abundantly and with great evolution of heat, by dry aniline, which then becomes darker in colour, and thickens into a crystalline magma, so that it requires to be heated in order to saturate it with the gas; the resinous mass which then solidifies on cooling consists of hydrochlorate of melaniline, $C^{26}N^3H^{13},HCl$:

$$2C^{12}NH^7 + C^2NCl = C^{26}N^3H^{14}Cl.$$

This product is however mixed with aniline-urea, the quantity of which is larger, in proportion as the exclusion of water has been less carefully attended to; aqueous chloride of cyanogen produces scarcely anything but this compound, mixed with hydrochlorate of aniline:

$$2C^{12}NH^7 + 2HO + C^2NCl = C^{14}N^2H^8O^2 + C^{12}NH^7,HCl.$$

(Hofmann, *Ann. Pharm.* 67, 130; 70, 129.) — [According to Cahours and Cloez (*Compt. rend.* 38, 354), dry chloride of cyanogen passed through an ethereal solution of aniline cooled with ice, forms nothing but cyaniline $C^{12}NCyH^6$, and hydrochlorate of aniline:

$$2C^{12}NH^7 + CyCl = C^{12}NH^7,HCl + C^{12}NCyH^6;$$

and by heating the mixture of cyaniline and hydrochlorate of aniline in alcoholic solution, a crystalline body is formed from which ammonia separates melaniline.] — 24. *Bromide of cyanogen* acts upon aniline like volatile chloride of cyanogen, converting it into hydrobromate of melaniline, and [in presence of water?] a small quantity of carbanilide. (Hofmann.) — 25. *Iodide of cyanogen* forms with aniline: iodaniline, a brown product containing iodine, and hydrocyanic acid. (Hofmann.) — 26. When *Hydropersulphocyanic acid* is heated with anhydrous aniline, the mixture melts and solidifies on cooling, into a mass which dissolves in boiling alcohol and ether, and when boiled with water containing a little potash, leaves a residue of sulphur, and yields a filtrate from which hydrochloric acid precipitates, together with sulphur, crystalline scales

which dissolve in boiling alcohol and ether. (Laurent & Gerhardt, *N. Ann. Chim. Phys.* 24, 198.)

27. The anhydrous mixture of *bromide of ethyl* and aniline does not decompose in the cold, but when heated in an apparatus which allows the volatilising bromide of ethyl to condense and flow back again, passes into spontaneous ebullition, turns brown, and then solidifies in a crystalline mass on cooling. If the aniline is in excess, the crystals consist of hydrobromate of aniline, while the mother-liquor contains ethylaniline together with free aniline:

$$2C^{12}NH^7 + C^4H^5Br = C^{12}NH^7,HBr + C^{16}NH^{11}.$$

With an excess of bromide of ethyl, the crystals consist of hydrobromate of ethylaniline, and the mother-liquor contains the same salt together with bromide of ethyl:

$$C^{12}NH^7 + C^4H^5Br = C^{16}NH^{11},HBr.$$

With a medium proportion, the two kinds of crystals are produced together. (Hofmann.) — 28. The solution of aniline in cyanuric ether (ix, 459), the formation of which is attended with considerable evolution of heat, solidifies, on cooling, in the form of crystalline ethylaniline-urea $C^{18}N^2H^{12}O^2$. (Wurtz, *Compt. rend.* 32, 417.) — The mixture of aniline and *mustard-oil* deposits after four months, four-sided tables, perhaps of $C^{12}N^2H^{12}S^2$, homologous with thiosinnamine. (Hofmann.) — ¶. On mixing 1 At. mustard-oil and 1 At. aniline in alcoholic solution (1 pt. aniline to 4 pts. of 90 per cent. alcohol), the mixture soon becomes heated, loses nearly all the odour of mustard-oil, and on cooling yields crystals consisting of a compound of the two bodies:

$$C^{12}NH^7 + C^8NH^5S^2 = C^{20}N^2H^{12}S^2.$$

(Zinin, *Ann. Pharm.* 84, 346.) ¶. — 29. A cold mixture of aniline and excess of bromide of amyl deposits after some days, crystals of hydrobromate of aniline, while the mother-liquor contains amylaniline together with bromide of amyl; but when the bromide of amyl is in very large excess, and the mixture is heated in the water-bath, hydrobromate of amylaniline separates from the bromide of amyl in the crystalline form. (Hofmann.)

$$2C^{12}NH^7 + C^{10}H^{11}Br = \underbrace{C^{22}NH^{17}}_{\text{amylaniline.}} + C^{12}NH^7,HBr;$$

and:

$$C^{12}NH^7 + C^{10}H^{11}Br = C^{22}NH^{17},HBr.$$

Aniline is not altered by being heated with carbolic acid to 250° for several days in a sealed tube. (Hofmann.)

30. Aniline, in combination with *organic acids*, is converted, by abstraction of 2 or 4 At. water, into conjugated compounds, some of which are also produced by aniline and certain chlorine-compounds belonging to the aldides, which form acids with water. The following classes are to be distinguished:

1. *Anilic acids*, corresponding to the amidogen-acids, compounds of 1 At. aniline and 1 At. of a bibasic acid *minus* 2 At. water: *e.g.*

$$\underbrace{C^{20}NH^{11}O^6}_{\text{succinanilic acid.}} = C^{12}NH^7 + C^8H^6C^8 - 2HO.$$

They dissolve but sparingly in water, more easily, however, than the following compounds :

2. *Anilides*, compounds analogous to the amides, either of 1 At. aniline with 1 At. of a monobasic acid *minus* 2 At. water, or of 2 At. aniline with 1 At. of a bibasic acid *minus* 4 At. water, the latter to be further distinguished as *Dianilides*: *e. g.*

$$2C^{12}NH^7 + C^4H^2O^8 - 4HO = \underbrace{C^{28}N^2H^{12}O^4}_{\text{oxanilide.}};$$

or of 1 At. aniline with 1 At. of a chlorine-compound *minus* 1 At. hydrochloric acid; *e.g.*

$$C^{12}NH^7 + \underbrace{C^{14}ClH^5O^2}_{\text{chlorobenzoyl.}} - HCl = \underbrace{C^{26}NH^{11}O^2}_{\text{benzanilide.}}$$

Many anilides volatilise when strongly heated. With melting hydrate of potash, they give off aniline, but not with boiling potash-ley. They are insoluble or sparingly soluble in water, but dissolve much more readily in alcohol.

3. *Anils*, compounds analogous to the imides (vii, 200), of 1 At. aniline and 1 At. of a bibasic acid *minus* 4 At. water : *e. g.*

$$C^{12}NH^7 + C^8H^6O^8 - 4HO = \underbrace{C^{20}NH^9O^4}_{\text{succinanil.}}.$$

They mostly volatilise when strongly heated. When boiled with aqueous ammonia, they take up 2 At. water, and are converted into a compound of ammonia with the corresponding anilic acid :

$$C^{20}NH^9O^4 + 2HO = \underbrace{C^{20}NH^{11}O^6}_{\text{succinanilic acid.}}.$$

With potash they behave like the anilides. They dissolve in alcohol much more readily than in water. (Laurent & Gerhardt, *N. Ann. Chim. Phys.* 24, 163; *comp.* Hofmann. *Ann. Pharm.* 73, 33.)

*Combinations*. When pure aniline obtained from the oxalate is shaken up with *water*, *Hydrated Aniline* is formed (probably containing only 1 At. water) and an *aqueous solution* containing very little aniline. (Hofmann.) Hydrated aniline when distilled, yields at first a distillate consisting chiefly of water, so that the last two-thirds are anhydrous. (Fritzsche.)—Aniline which has not been freed from the offensive-smelling substance (odorine) by combination with oxalic acid (p. 248), dissolves much more abundantly and forms a lower layer consisting of a much more saturated solution of aniline in water, and an upper layer of hydrated aniline containing a much larger proportion of water, viz. 30 p.c. (more than 4 At. water), and becomes turbid even at the heat of the hands. — Pure aniline dissolves in water more abundantly the higher the temperature, so that a solution saturated at a boiling heat becomes milk-white on cooling. From a solution prepared in the cold, the aniline is separated by caustic potash or soda or their carbonates, also by common salt and sulphate of magnesia; and ether dissolves it out from the water. But the cold-saturated aqueous solution of aniline still containing odorine, becomes turbid even at the heat of the hand, and when boiled, yields a large quantity of hydrated aniline which rises to the surface; it is also rendered turbid by 4 drops of sulphuric or oxalic acid, and

becomes clear only on the addition of a large quantity, whereas the solution of pure aniline remains clear when thus treated. (Hofmann.) — Aniline dissolves readily in water (Runge); sparingly (Fritzche); not at all. (Zinin.)

Aniline dissolves *phosphorus* with tolerable facility (Hofmann), *sulphur* very abundantly with the aid of heat, and deposits it in the crystalline form on cooling (Fritzsche, Hofmann); it mixes in all proportions with *sulphide of carbon*. (Hofmann.)

Aniline combines with acids, the combination being attended with rise of temperuture (Hofmann) and neutralisation of the acid (Runge), and forms the *Aniline-salts.* It precipitates the salts of alumina, zinc-oxide, ferrous oxide and ferric oxide, but not those of magnesia, chromic oxide, manganous oxide, cobalt-oxide or nickel-oxide; neither does it form any precipitate with mercurous nitrate or nitrate of silver. (Hofmann.) Its compounds with inorganic oxygen-acids contain water as an essential constituent. (Zinin, Fritzsche, Hofmann.) Most aniline-salts crystallise readily. (Unverdorben, Zinin.) — Sometimes the offensive-smelling substance (the odorine) in aniline which has not been separated from the oxalate, interferes with the crystallisation. (Hofmann.) — The salts are mostly colourless and inodorous. (Hofmann.) When exposed to the air, they assume a rose colour, especially when moist. (Hofmann.) Fixed alkalis separate the aniline from them in oily drops; so does ammonia at ordinary temperatures, whereas at higher temperatures the ammonia is expelled by the aniline. (Hofmann.) From the dried salts, potassium-amalgam eliminates hydrogen and aniline. The aniline-salts, especially the hydrochlorate and nitrate, give, with chloride of lime containing excess of lime, an azure-blue solution (p. 251); this coloration is least intense with the acetate. To firwood or elder-pith, in consequence of the presence of a substance which may be extracted by water or alcohol (but not to paper, linen, cotton, silk, or wool), they impart a deep yellow colour, which is not destroyed by chlorine, and is still perceptible in a solution containing only $\frac{1}{500000}$ of aniline. (Runge.) — The salts of naphthalidam produce this colour with greater intensity, those of leucol produce it after a while, whereas those of sinnamine, conine and chinoline, yield only a pale yellow colour. (Hofmann.)

Aniline does not combine with carbonic acid. (Hofmann.)

*Ordinary Phosphate of Aniline.* — *a. Bibasic.* — Concentrated phosphoric acid supersaturated with aniline, solidifies immediately in a white crystalline mass, which, after being pressed, dissolved in a large quantity of boiling alcohol, strained through a hot filter, and cooled, yields flesh-coloured, nacreous, inodorous laminæ, which slightly redden litmus; they must be pressed between paper and dried on a warm tile. At 100° they turn red and give off aniline; melt at a stronger heat, and finally leave metaphosphoric acid (coloured, according to Gerhardt, by the carbonisation of a small quantity of aniline) while the aniline volatilises. They dissolve readily in water and ether, sparingly in cold alcohol, but so abundantly in hot alcohol, that the liquid solidifies on cooling. (E. C. Nicholson, *Ann. Pharm.* 59, 213.)

| | *Crystals.* | | Nicholson. |
|---|---|---|---|
| 24 C | 144·0 | 50·63 | 50·16 |
| 2 N | 28·0 | 9·85 | |
| 17 H | 17·0 | 5·97 | 6·10 |
| 3 O | 24·0 | 8·44 | |
| $PO^5$ | 71·4 | 25·11 | 24·86 |
| $2(C^{12}NH^7,HO),Aq,cPO^5$ | 284·4 | 100·00 | |

*b. Monobasic.* The aqueous solution of the salt *a* mixed with phosphoric acid, till it no longer precipitates chloride of barium, yields, in a few hours, after evaporation over the water-bath, white silky needles, which must be cooled with ether and dried on a warm tile; they turn red in the air, and dissolve readily in water, alcohol and ether; in water, however, the salt *a* is formed at the same time. (Nicholson.)

| *Crystals.* | | | Nicholson. |
|---|---|---|---|
| 12 C | 72·0 | 37·62 | 37·86 |
| N | 14·0 | 7·32 | |
| 10 H | 10·0 | 5·22 | 5·44 |
| 3 O | 24·0 | 12·54 | |
| $PO^5$ | 71·4 | 37·30 | 37·12 |
| $C^{12}NH^7,HO,2Aq,cPO^5$ | 191·4 | 100·00 | |

*Pyrophosphate of Aniline.* — Concentrated pyrophosphoric acid obtained by decomposing pyrophosphate of lead with sulphuretted hydrogen, forms with excess of aniline, a gelatinous hardening precipitate which is a mixture of *bibasic* and *monobasic* salt. The former cannot be prepared in the pure state; but the monobasic salt is obtained, by heating the mixture till solution takes place, supersaturating with acid, and evaporating over the water-bath, in the form of a needle-shaped mass which solidifies on cooling; it must be pressed between paper, washed with ether, and dried in vacuo. The silky needles resemble sulphate of quinine, are strongly acid, turn red on exposure to the air, both in the solid state and in solution, and are soluble in water, but quite insoluble in alcohol and ether. (Nicholson.)

| *Crystals dried in vacuo.* | | | Nicholson. |
|---|---|---|---|
| 12 C | 72·0 | 39·47 | 39·42 |
| N | 14·0 | 7·68 | |
| 9 H | 9·0 | 4·93 | 5·56 |
| 2 O | 16·0 | 8·77 | |
| $PO^5$ | 71·4 | 39·15 | 38·85 |
| $C^{12}NH^7,HO,bPO^5 + Aq$ | 182·4 | 100·00 | |

*Metaphosphate of Aniline.* — The concentrated solution of glacial phosphoric acid added in large excess to aniline or to its solution in alcohol or ether, throws down a white jelly, which must be washed on the filter with ether, till the odour of aniline disappears, and dried in vacuo over oil of vitriol. White amorphous mass, which reddens litmus, becomes glutinous and rose-coloured on exposure to the air, and dissolves in water, but is quite insoluble in alcohol and ether. The aqueous solution is altered by boiling, in consequence of the formation of ordinary phosphoric acid; it dissolves metaphosphate of silver, but afterwards turns red on boiling, the silver-salt being partly reduced. (Nicholson.)

| *Dried in vacuo.* | | | Nicholson. |
|---|---|---|---|
| 12 C | 72·0 | 41·52 | 41·33 |
| N | 14·0 | 8·08 | |
| 8 H | 8·0 | 4·61 | 4·55 |
| O | 8·0 | 4·61 | |
| $aPO^5$ | 71·4 | 41·18 | 41·11 |
| $C^{12}NH^7,HO,aPO^5$ | 173·4 | 100·00 | |

*Sulphite of Aniline.* — When sulphurous acid gas is absorbed by aniline, crystals are formed. (Hofmann.)

*Sulphate of Aniline.* — Dilute sulphuric acid removes the odour of aniline, and yields on evaporation, even when the acid is in excess, crystals of the neutral salt, which may be washed with cold absolute alcohol, crystallise in large laminæ from boiling absolute alcohol, and taste of aniline. (Unverdorben.) — The ethereal solution of the oily mixture of aniline, leucol, and a small quantity of neutral oil (p. 248), solidifies when mixed with a small quantity of oil of vitriol, forming a white crystalline magma, which may be freed from leucol by washing with cold absolute alcohol, then dissolved in boiling alcohol, separated by filtration from a small quantity of sulphate of ammonia, and obtained in crystalline crusts by spontaneous evaporation. (Hofmann.) — The concentrated alcoholic solution of aniline solidifies with oil of vitriol, into a white mass, which crystallises from boiling alcohol, in white silvery laminæ having a sharp, slightly acid and bitter taste. (Zinin.) — Dilute sulphuric acid supersaturated with aniline yields, on evaporation, a white crystalline mass which is permanent in the air and reddens litmus. (Runge.) — The crystals, when exposed to the air, acquire the odour of aniline, a formation of fuscine taking place at the same time (Unverdorben); they also turn red on exposure to the air, especially if moist. (Zinin.) — The crystals may be dried at 100° without decomposition, beyond the production of a slight brown colour. (Hofmann.) When heated, they give off, first a little water, then aniline, and leave an acid salt, which, when further heated, leaves a residue of charcoal, and yields a mixed crystalline sublimate of sulphite of aniline, ammonia, and odorine. (Unverdorben.) At a stronger heat, they quickly become carbonised and give off water, sulphurous acid, and a small quantity of ammonia. (Runge.) They first give off aniline, then sulphuric acid, and leave a tumefied, slowly combustible charcoal. (Hofmann.) When set on fire on platinum foil, they burn with a reddish sooty flame, and leave a large quantity of charcoal. (Zinin.) The salt dissolves very readily in water and alcohol. (Zinin.) The aqueous solution saturated at a boiling heat solidifies on cooling; dilute alcohol dissolves a large, cold absolute alcohol a small quantity, hot absolute alcohol a large quantity, and ether none. (Unverdorben, Hofmann.)

| | *At* 100°. | | Zinin. | Hofmann. |
|---|---|---|---|---|
| 12 C | 72 | 50·71 | 50·21 | |
| N | 14 | 9·86 | | |
| 8 H | 8 | 5·63 | 5·90 | |
| O | 8 | 5·63 | | |
| $SO^3$ | 40 | 28·17 | 28·99 | 28·67 |
| $C^{12}NH^7,HO,SO^3$. | 142 | 100·00 | | |

*Hydriodate of Aniline.* — Needles, which dissolve very readily in water and alcohol, less readily in ether. (Hofmann.)

| | *Needles.* | | Hofmann. |
|---|---|---|---|
| $C^{12}NH^7$ | 93 | 42·27 | |
| HI | 127 | 57·73 | 57·53 |
| $C^{12}NH^7,HI$ | 220 | 100·00 | |

*Hydrobromate of Aniline.*—Sublimes without decomposition, even when rapidly heated. (Hofmann.)

*Hydrochlorate of Aniline.*—Hydrochloric acid held over aniline, forms fumes, according to Hofmann, but according to Runge it does not.—Hydrochloric acid supersaturated with aniline yields by evaporation, crystals which sublime and melt at the same time, redden litmus, dissolve very readily in water, alcohol and ether, and when mixed with nitre, blacken at a gentle heat, with an odour like that which is emitted during the sublimation of indigo. (Runge.) The salt, which dissolves very readily in water and alcohol, crystallises from alcohol in white laminæ, which sublime readily and without decomposition, in the form of a loosely coherent powder, consisting of delicate needles, and having a saline bitter taste. (Zinin.) With strong hydrochloric acid, pure aniline solidifies immediately into a crystalline pulp. The salt crystallises from water or alcohol in slender needles which have a pungent taste, and sublime without decomposition. Aniline not purified by combination with oxalic acid, and still retaining an unpleasant odour, does not yield crystals with strong hydrochloric acid, but solidifies after a while into a thick uncrystallisable syrup; and its solution in ether immediately deposits a similar syrup when hydrochloric acid gas is passed through it. (Hofmann.)

| | *Crystals.* | | Fritzsche. | Zinin. |
|---|---|---|---|---|
| 12 C | 72·0 | 55·64 | | 55·08 |
| N | 14·0 | 10·82 | | |
| 8 H | 8·0 | 6·18 | 6·05 | 6·42 |
| Cl | 35·4 | 27·36 | 27·18 | 26·58 |
| $C^{12}NH^7,HCl$ | 129·4 | 100·00 | | |

*Nitrate of Aniline.*—Nitric acid supersaturated with aniline yields on evaporation, colourless, non-deliquescent needles, which redden litmus, blacken at 100°, only in presence of free acid, or after being moistened with protochloride of copper; and when heated alone above 100°, are quickly converted, with slight detonation, into a black mass. (Runge.)—A mixture of aniline and dilute nitric acid yields, after a while, bundles of needles, which must be purified by pressure between paper. The red mother-liquor yields blue efflorescences. With moderately strong acid, aniline solidifies into a rose-coloured crystalline mass; but with stronger acid, it is decomposed, and suddenly assumes a darker colour. The crystals melt when cautiously heated, and are converted, with slight decomposition, into a colourless vapour, which condenses in delicate crystalline flowers. But when rapidly heated on platinum foil, they give off aniline and become carbonised. (Hofmann.)

Aniline produces, both with *terchloride of antimony* and with *bichloride of tin* copious white curdy precipitates which crystallise from hot hydrochloric acid. (Hofmann.)

*Fluoride of Silicium with Aniline.*—93 pts. of aniline absorb 63.3 pts. of gaseous fluoride of silicium, and form a pale yellow mass, which when washed with ether, well boiled with alcohol, pressed, dried and sublimed, is converted into a very light crust. This product contains 59·52 p. c. C, 4·40 H, and when ignited with excess of oxide of lead, which expels the aniline, leaves 42·2 p. c. F and $SiO^2$. Water separates from it gelatinous silica. It dissolves sparingly in boiling alcohol, and crystallises from it in laminæ having a very strong lustre. (Laurent & Delbos, *N. Ann. Chim. Phys.* 22, 101, abstr. *N. J. Pharm.* 10, 309.)

*Sulphate of Copper with Aniline.—Sulphate of Cupranilium.* $C^{12}NH^7Cu,SO^4$. [anilium = $C^{12}NH^8$]. —First observed by Hofmann.—Obtained by precipitating a dilute solution of sulphate of copper with aniline suspended in water and mixed with a sufficient quantity of alcohol to render the liquid clear. Pistachio-green crystalline scales, which must be washed with water and dried, first by exposure to the air, then at 100°. When thus prepared, they contain 18·5 p. c. copper, and therefore consist of $C^{12}NH^7,CuO,SO^3$. When heated, they give off half their aniline, and leave a black mixture of cupric oxide and cupric anilosulphate, which last may be extracted by water, and recognised by the red colour which it produces with chromic acid :

$$2C^{12}NH^7CuSO^4 = C^{12}NH^7 + C^{12}NH^6CuS^2O^6 + CuO + HO.$$

When the scales are boiled with water, aniline volatilises and sulphate of aniline dissolves, while bibasic cupric sulphate remains. (Gerhardt) :

$$2C^{12}NH^7CuSO^4 + HO = C^{12}NH^7 + C^{12}NH^8SO^4 + 2CuO,SO^3.$$

With protochloride of copper, aniline forms a precipitate of similar character, but which very easily turns black. (Hofmann.)

*Chloride of Mercury with Aniline.*—The crystalline precipitate which aniline forms with corrosive sublimate was first observed by Zinin.

*a. With* 1 *At. Chloride of Mercury.* — *Chloride of Mercuranilium* $C^{12}NH^7Hg,Cl$. Alcoholic aniline in excess is precipitated by alcoholic corrosive sublimate. Nacreous precipitate, which must be collected on a filter and washed with a small quantity of alcohol. It gives off a small quantity of aniline even at 60°, and turns yellowish. (Gerhardt.)

| | | | | Gerhardt. |
|---|---|---|---|---|
| 12 C | 72·0 | .... | 31·52 | 31·2 |
| N | 14·0 | .... | 6·13 | |
| 7 H | 7·0 | .... | 3·07 | |
| HgCl | 135·4 | .... | 59·28 | |
| $C^{12}NH^7HgCl$ | 228·4 | .... | 100·00 | |

*b. With* 3 *At. Chloride of Mercury.*—Rises to the surface as a pasty mass when aniline is mixed with [excess of ?] aqueous corrosive sublimate; on mixing the alcoholic solutions, it is precipitated in the form of a soft white powder, which soon becomes crystalline. It must be washed with water. When boiled with water, it turns lemon-yellow, with evolution of a small quantity of aniline, and partial solution of the salt which crystallises out without alteration on cooling. In a small quantity of hot hydrochloric acid, it dissolves partially and melts into a heavy red oil; in a larger quantity it dissolves completely, and yields white crystals on cooling. In cold water it dissolves very sparingly; slightly also in boiling alcohol, from which it crystallises on cooling. (Hofmann.) Of the same composition also are probably the needles which Gerhardt obtained by further addition of corrosive sublimate to the alcoholic liquid filtered from the salt *a*; this liquid when boiled with alcohol, yielded an orange-yellow residue, and a dark yellow filtrate from which a mixture of colourless and orange-yellow crystals was deposited on cooling.

| | | | | | | |
|---|---|---|---|---|---|---|
| | | | | | | Hofmann. |
| 12 C | 72·0 | .... | 14·43 | ........ | | 14·20 |
| N | 14·0 | .... | 2·81 | | | |
| 7 H | 7·0 | .... | 1·40 | | | |
| 3 Hg | 300·0 | .... | 60·09 | ........ | | 60·63 |
| 3 Cl | 106·2 | .... | 21·27 | ........ | | 20·36 |
| $C^{12}NH^7,3HgCl$ | 499·2 | .... | 100·00 | | | |

May be regarded as $C^{12}NH^7HgCl,2HgCl$.

With *terchloride of gold*, aniline forms a red-brown, and hydrochlorate of aniline a yellow precipitate, the colour of which quickly changes to dingy red-brown. (Hofmann.)

*Chloroplatinate of Aniline.* — Aniline dissolved in a large quantity of hydrochloric acid quickly solidifies with aqueous bichloride of platinum, into an orange-yellow crystalline pulp: if the solution of hydrochlorate of aniline was previously mixed with an equal volume of alcohol, slender needles are more slowly formed on addition of the platinum-solution. If the aniline in the mixture predominates over the hydrochloric acid, it turns brown, in consequence of the formation of decomposition-products. The crystals are washed with a cold mixture of ether and alcohol, and dried. They dissolve sparingly in a mixture of ether and alcohol, but not in pure ether. (Hofmann.) The brownish-yellow precipitate sparingly soluble in water and alcohol, which Zinin obtained by adding pure aniline to solution of platinum appears from analysis, after careful washing with ether and alcohol, and drying at 100°, to be identical with this compound.

| *At* 100°. | | | | | Hofmann. | | Zinin. |
|---|---|---|---|---|---|---|---|
| 12 C | 72·0 | .... | 24·07 | ........ | 24·15 | | |
| N | 14·0 | .... | 4·68 | | | | |
| 8 H | 8·0 | .... | 2·70 | ........ | 2·67 | | |
| Pt | 99·0 | .... | 33·06 | ........ | 32·89 | .... | 32·43 |
| 3 Cl | 106·2 | .... | 35·49 | ........ | 34·82 | | |
| $C^{12}NH^8Cl,PtCl^2$ | 299·2 | .... | 100·00 | ........ | 100·00 | | |

With *chloride of palladium*, aniline forms a precipitate of a fine orange-yellow colour. (Hofmann.)

*Sulphocyanate of Aniline.*—Aqueous hydrosulphocyanic acid saturated with aniline deposits on evaporation, red oily drops which gradually solidify in the crystalline form. The crystalline mass melts when gently heated; then gives off sulphuretted hydrogen and sulphide of ammonium, with violent ebullition; and when more strongly heated, yields an oily distillate of sulphide of carbon and sulphide of ammonium together with sulphocarbanilide, and leaves a pale resinous residue :

$$2(C^{12}NH^7,C^2NHS^2) = \underbrace{C^{26}N^2H^{12}S^2}_{\text{sulphocarbanilide.}} + \underbrace{C^2N^2H^4S^2}_{\text{sulphocyanide of ammonium.}}.$$

But the latter is further resolved at the given temperature into sulphide

of carbon, sulphide of ammonium, and a residue of mellone, to which however an aniline-compound adheres. (Hofmann.):

$$2C^{12}NH^7 + C^2NHS^2 = C^{26}N^2H^{12}S^2 + NH^3. \quad \text{(Laurent \& Gerhardt.)}$$

*Acetate of Aniline.* — Does not crystallise; may be distilled over with water. (Runge.)

*Oxalate of Aniline.* — *Bibasic.* — The alcoholic solutions of aniline and oxalic acid, deposit when mixed, a white powder, which, after washing with alcohol, crystallises from hot water in long needles. (Fritzsche.) The crystalline pulp obtained on mixing aniline with alcoholic oxalic acid, crystallises on cooling from solution in the smallest possible quantity of boiling water, in oblique rhombic prisms united in stellate groups, whose solution reddens litmus. (Hofmann.) From water the salt crystallises in broad laminæ; from alcohol, in needles united in stellate groups. The precipitate formed in aniline by excess of oxalic acid, after being washed with water and several times recrystallised, is likewise a needle-shaped bibasic salt containing 61·01 p. c. C. (Hofmann.) At 100°, the crystals give off aniline slowly but continuously, and assume a yellow colour. The aqueous solution quickly becomes coloured on exposure to the air, and deposits a brown-red powder. (Hofmann.) The crystals when heated, give off aniline and water, and then sublime in the form of an acid salt. They decompose at a temperature somewhat above 100°, fusing, boiling, and giving off aniline and carbonic acid, with which, between 160° and 180°, there is likewise associated carbonic oxide (and, according to Hofmann, a trace of anilocyanic acid). At this temperature, there remains a clear red liquid, which, on cooling, solidifies into a buttery mixture of oxanilide and formanilide:

$$2C^{12}NH^7,C^4H^2O^8 = \underbrace{C^{28}N^2H^{12}O^4}_{\text{oxanilide.}} + 4HO;$$

and:

$$2C^{12}NH^7,C^4H^2O^8 = \underbrace{C^{14}NH^7O^2}_{\text{formanilide.}} + C^{12}NH^7 + 2CO^2 + 2HO. \quad \text{(Gerhardt.)}$$

¶ Perfectly pure oxalate of aniline may be heated in the oil-bath to temperatures between 160° and 180°, without fusing, and without production of formanilide, the residue, which is perfectly white and crystalline consisting wholly of oxanilide. But oxalate of aniline in a less pure state, melts and yields formanilide as well as oxanilide (Piria, *Il nuovo Cimento*, 2, 305; *Instit.* 1856, 224). ¶. — The crystals are less easily soluble in water, alcohol and ether than other aniline-salts (Runge); they dissolve readily in water, sparingly in absolute alcohol, not at all in ether. (Hofmann.)

| *Crystals.* | | | Fritzsche. | Hofmann. |
|---|---|---|---|---|
| 28 C | 168 | 60·87 | 61·67 | 61·25 |
| 2 N | 28 | 10·15 | 10·21 | |
| 16 H | 16 | 5·79 | 5·77 | 6·05 |
| 8 O | 64 | 23·19 | 22·35 | |
| $2C^{12}NH^7,C^4H^2O^8$ | 276 | 100·00 | 100·00 | |

¶. *Mellitate of Aniline.* $C^{12}NH^7,C^8H^2O^8$. — When aqueous aniline is shaken up with a solution of mellitic acid, a turbid liquid is obtained which gradually deposits scaly laminæ resembling those of benzoic acid. The crystals dissolve readily in water; alcohol also dissolves them when hot, but the solution does not yield crystals. They do not undergo any alteration at 100°, but at 105°, they turn yellow and give off aniline. (Karmrodt, *Ann. Pharm.* 81, 172.) ¶.

*Butyrate of Aniline.* — Oily liquid, easy to distil, sparingly soluble in water. (Unverdorben.)

*Succinate of Aniline.* — Thin, oblique rectangular prisms, of a pale rose colour. (Gerhardt.)

*Tartrate of Aniline.* — The aqueous acid solidifies with aniline. The salt crystallises from hot water in needles. (Hofmann.)

¶ *Sulphobenzolate of Aniline* $C^{12}H^5(C^{12}NH^8),S^2O^6$. — *Sulphophenylate of Aniline.* — Obtained by dropping aniline into a hot solution of sulphobenzolic acid. (p. 155.) Crystallises in long silky needles arranged in stellate groups, and generally exhibiting a reddish tint. They melt at 201°, and the fused salt solidifies in a stellate crystalline mass; it sublimes below the melting point in colourless crystals. Dissolves readily in water and alcohol, sparingly in ether. (Gericke, *Ann. Pharm.* C, 217.) ¶

*Picrate of Aniline.* — The lemon-yellow precipitate which an excess of alcoholic picric acid forms with aniline, dissolves in boiling alcohol, and crystallises on cooling. (Hofmann.)

Aniline mixes in all proportions with *wood-spirit, alcohol, ether, aldehyde* and *acetone.* (Hofmann.) Ether abstracts it from its aqueous solution. (Runge.)

Aniline mixes in all proportions with oils both fixed and volatile; it dissolves common camphor and colophonium, but not copal or caoutchouc. It coagulates white of egg. (Hofmann.)

## Picoline.

$$C^{12}NH^7 = C^{12}AdH^3,H^2. ?$$

UNVERDORBEN. *Pogg.* 8, 259 and 480; 11, 59.

ANDERSON. *N. Ed. Phil. J.* 41, 146 and 291; also *Ann. Pharm.* 60, 86; also *J. pr. Chem.* 40; 481.—*Phil. Mag. J.* [3], 33, 185; also *J. pr. Chem.* 45, 166. — Further: *Ed. Phil. Trans.* 21, Pt. I. 219; *Phil. Mag. J.* [4], 9, 214; *Ann. Pharm.* 94, 358.

*Odorine.* — The base *Odorine,* discovered in 1826 by Unverdorben in bone-oil,— together with three other less volatile alkaloïds, reserved for more precise investigation, and named from *Oleum animale, Animine, Olanine,* and *Ammoline,*—was obtained in greater purity and more exactly investigated by Anderson in 1846, as *Picoline.*

*Formation.* 1. In the dry distillation of bones, and in smaller quantity, in that of coal [also, of certain varieties of bituminous shale

(C. G. Williams, *Chem. Soc. Qu. J.* 7, 97)]. The bones, from which the greater part of the fat is generally removed by boiling with water, yield by dry distillation, an oil, which when separated from the watery distillate and rectified, is of a greenish black-brown colour; exhibits a brown colour by transmitted light only in thin layers; has a density of 0·970; an offensive ammoniacal odour; diffuses vapours which impart a dark purple colour to deal shavings moistened with hydrochloric acid (the pyrrhol described by Runge, *Gilb.* 31, 67); yields to alkalis a large quantity of hydrochloric acid and an acid oil [carbolic acid ?], while to acids, it yields ammonia, alkaloids, and a neutral oil which separates in orange-yellow resinous flakes, slowly in the cold, immediately when heated, the quantity of this oil being greater, the more concentrated the acid. In the rectification of the oil, there passes over, first an ammoniacal watery liquid containing volatile alkaloid in solution, then a transparent, pale yellow very volatile oil, containing petinine, odorine, and aniline, and displacing the watery liquid more and more as the distillation proceeds:— then when $\frac{2}{5}$ of the whole have passed over, and the heat has increased, an oil containing the less volatile alkaloids, which becomes continually thicker and of a darker brown colour, and ultimately green by reflected and red-brown by transmitted light; — till at length, when the bottom of the retort has risen to a red heat, a quantity of spongy charcoal is formed and water and carbonate of ammonia escape. Crude bone-oil contains about 0·75 p. c. of the more volatile and from 2 to 3 per cent. of the less volatile alkaloids. (Anderson.)

2. By distilling piperine intimately mixed with 4 pts. of soda-lime, at temperatures between 150° and 160°. (Wertheim, *Ann. Pharm.* 70, 62). — Cinchonine distilled with hydrate of potash also yields a number of volatile bases, among which picoline is found in small quantity. (C. G. Williams, *Ed. Phil. Trans.* xxi, Pt. 2.)

*Preparation.* 1. The oily mixture obtained from bone-oil in the manner described for the preparation of petinine (x, 150), and dehydrated by means of hydrate of potash, yields between 71° and 100°, a distillate consisting chiefly of petinine, then between 132° and 137° principally picoline, and from 151° to the end, chiefly aniline. By repeatedly rectifying the distillate obtained between 132° and 137°, and separating each time the first and last portions, picoline is obtained in a state of purity. (Anderson.)

2. The oil which passes over in the rectification of coal-tar is shaken up with sulphuric acid, to dissolve out the bases and remove the naphthalin and the oil which turns brown on exposure to the air; the sulphuric acid liquid neutralised with the impure ammonia obtained by rectifying the watery distillate of coal tar, and distilled, whereupon there passes over with the first portions of water, a dark brown, thickish, oily mixture, sinking in water, having an offensive pungent odour, and consisting of picoline, aniline, pyrrhol, leucol and a thick heavy neutral oil; this oily mixture, together with the supernatant watery distillate, carefully rectified, till only one-fourth (containing the heavy neutral oil) remains; the distillate, consisting of aqueous picoline and a supernatant oil, strongly supersaturated with dilute sulphuric acid, whereby its odour is considerably altered; the acid mixture, which gives off all the pyrrhol in the state of aqueous solution, distilled; the residue in the retort supersaturated with potash, and the distillation continued, whereby bases are obtained, partly dissolved in water, partly floating on the

surface in the form of an oil; the entire distillate left at rest in contact with fragments of caustic potash, by the gradual solution of which, the picoline loses its solubility in water, and is thrown up to the surface in the form of a pale yellow oil containing from 30 to 40 per cent. of water; this oily layer removed with the pipette, and repeatedly treated with solid potash, which must be renewed as often as it gets wet; the oil thus dehydrated, consisting of picoline and aniline, distilled, the receiver being changed as soon as a drop of the distillate turns blue when mixed with aqueous chloride of lime (and therefore contains aniline); and the distillation still continued, whereby a mixture is obtained consisting of picoline and a continually increasing quantity of aniline. The first portion of picoline which passes over, is free from aniline, and after being dehydrated with solid potash, and brought by fractional distillation to the boiling point 133·3°, is pure. (Anderson.)

3. *Preparation of Odorine, Animine and Ammoline.*—Bone-oil is freed from the whole of the watery liquid, and mixed with dilute sulphuric acid as long as effervescence ensues; at least an equal quantity then added, in order to convert all the sulphates into acid salts; the liquid diluted with water amounting to half the oil; decanted after being stirred; shaken, and set aside for several hours; then strained through linen, and boiled for three hours in a porcelain basin with water renewed as it evaporates —whereupon it assumes a dark-brown colour and deposits resin in consequence of oxidation of the empyreumatic oil; the liquid separated therefrom mixed with $\frac{1}{40}$ pt. of nitric acid; evaporated to $\frac{1}{4}$; then brought back to its former capacity by addition of water; saturated in a glass retort with carbonate of soda, till it scarcely reddens litmus; and distilled in a glass retort, as long as the liquid which passes over smells of odorine and animine, which bases pass over perfectly free from ammonia.—*a.* The *distillate* is mixed with a quantity of sulphuric acid sufficient to remove its odour, then with another equal quantity, in order to form acid salts; evaporated in the water-bath till it becomes thickish; poured gradually, so that the heat may not become too great, into a retort containing excess of quicklime; and distilled, whereupon anhydrous odorine and animine pass over. This mixture shaken up with 3 pts. of water, yields, with separation of a large quantity of pure animine, a solution containing all the odorine and a little animine. By adding to this liquid, a boiling aqueous solution of corrosive sublimate in excess, a compound of chloride of mercury with animine separates, even while the liquid is hot, as an oil which solidifies on cooling, whereas the compound of chloride of mercury with odorine remains dissolved while the liquid is hot, and crystallises on cooling. On collecting each of these double salts separately, and distilling with potash, animine is obtained from the one and odorine from the other.—*b.* The *liquid remaining* in the retort is filtered from the resin, mixed while constantly boiling with carbonate of soda as long as ammonia escapes, and evaporated with excess of carbonate of soda; and the brown oil which then separates, and is a compound of ammoline and fuscine, is washed with water and distilled, whereupon the ammoline passes over: if not quite colourless, it must be purified by redistillation. It then still contains, besides traces of hydrocyanic acid, ammonia, odorine and alanine, an oil having a spirituous, radish-like odour, soluble in 20 pts. of hot water, and easily volatilised therewith, so that all these bodies may be easily removed from the *ammoline* by boiling with water. (Unverdorben.)

4. *Preparation of Odorine, Animine, and Olanine.* — Dippel's oil is exactly neutralised with nitric acid till the alkaline reaction is destroyed; the decanted oil distilled in the water-bath, as long as the distillate is soluble in water, and therefore consists of pure odorine; and then with a fresh receiver, as long as a mixture of odorine and animine which becomes turbid on addition of water, passes over, while $\frac{1}{20}$ of the whole remains as a mixture of animine and olanine. (Unverdorben, in Berzelius *Lehrb. Ausg.* v, 5, 248.) The second distillate, when shaken up with an equal quantity of water, separates into *animine* and an aqueous solution to be further separated (upwards), and consisting of *odorine* with a small quantity of *animine.* The residue in the retort, washed with 20 pts. of cold water, gives up to that liquid the rest of the *animine,* while the *olanine* remains undissolved. (Unverdorben.)

5. Pure odorine is likewise obtained by passing the vapour of Dippel's oil through a red-hot tube, distilling the condensed liquid with $\frac{1}{8}$ pt. of hydrate of potash and 6 pts. of water, supersaturating the distillate with sulphuric acid, boiling to expel the volatile oil, and then distilling with oxide of lead or oxide of copper, whereupon aqueous odorine passes over. (Unverdorben.)

An impure odorine is obtained by distilling oil of hartshorn with hpdrate of potash, &c. — If the odorine is contaminated with ammonia, its compound with tartaric acid must be dissolved in absolute alcohol, which leaves the ammonia-salt undissolved. — To obtain odorine quite free from empyreumatic oil, the compound of chloride of copper with odorine is prepared (p. 269), and distilled with potash. (Unverdorben.)

Compare Reichenbach's observations (*Schw.* 61, 464; 62, 46) on Unverdorben's methods of preparation, and Unverdorben's observations in reply. (*Schw.* 65, 314.)

*Properties.* Transparent, colourless, very thin oil, not solidifying at 0°; of sp. gr. 0·955 at 10°; boiling constantly at 133·3°; having an obstinately persistent, somewhat aromatic, strongly penetrating, and in the dilute state, peculiar rancid odour, and a fiery, sharp taste, extremely bitter in the dilute state. Blues litmus, but does not change the colour of red cabbage. Produces fumes with hydrochloric acid. It does not colour firwood or elder-pith yellow when mixed with acids, and remains colourless with chloride of lime, unless the presence of pyrrhol produces a brown colour. (Anderson.) — Colourless oil, lighter and somewhat less mobile than water; does not solidify at — 25°; volatile; produces fumes when hydrochloric, nitric, or acetic acid is held over it; has a peculiar ammoniacal odour, which, after the substance has been purified by preparation from its compound with chloride of copper, no longer resembles that of bone-oil, but that of *Syringa vulgaris*; it is not poisonous, blues litmus, and turns violets green. (Unverdorben.)

| | | | Anderson. |
|---|---|---|---|
| 12 C | 72 | 77·42 | 77·17 |
| N | 14 | 15·05 | |
| 7 H | 7 | 7·53 | 7·69 |
| $C^{12}NH^7$ | 93 | 100·00 | |

Isomeric, therefore, with aniline; it should perhaps be regarded as $C^{12}AdH^3,H^2$, which however presupposes the existence of the nucleus $C^{12}H^4$, not otherwise known.

*Decompositions.* Picoline does not turn brown or undergo any change in vessels containing air. — 1. Picoline absorbs chlorine gas in considerable quantity, deposits colourless crystals of hydrochlorate of odorine, then assumes a dark brown colour, and is converted into a resin; and this, when suspended in water and further treated with chlorine, yields by distillation, first a crystalline substance which passes over with the water, and then another after the water has gone over. (Anderson.) — Chlorine gas passed in excess over picoline, produces thick fumes and a dense yellow liquid, from which water (taking up $\frac{2}{3}$ of the picoline in the form of hydrochlorate of picoline, no longer decomposible by chlorine) precipitates a yellow body, from which potash extracts a brownish yellow powder, leaving a resin which dissolves only in oil of vitriol or in picoline. (Unverdorben.) — 2. *Bromine* in excess immediately forms with picoline a copious reddish precipitate, which, if left over night, collects into a non-basic oil insoluble in water, but readily soluble in alcohol and ether. (Anderson.) — With *iodine* and water, picoline forms hydriodate of picoline, a brown powder soluble in potash, and an extractive matter soluble in alcohol and ether, but insoluble in water. (Unverdorben.) — 3. Picoline dissolves in *nitric acid* without any blue coloration, but the mixture, when heated, slowly gives off nitrous vapours, and, if evaporated after long digestion, yields rhombic tables [of nitrate of picoline ?], but no picric acid. (Anderson.) — With aqueous chromic acid, it exhibits no change of colour, even on boiling, but merely yields a small quantity of yellow powder. (Anderson.)

*Combinations.* Picoline mixes in all proportions with water, but is separated therefrom on saturating the liquid with potash and with many alkaline salts. (Anderson.) Miscible with water in all proportions. (Unverdorben.)

Picoline precipitates the hydrochlorates of uranic, stannic and ferric oxide, but is separated from its salts by all basic metallic oxides. (Unverdorben.) *Picoline-salts* are mostly crystallisable, but do not crystallise so easily or so finely as the aniline-salts; the best crystals are obtained by evaporating the aqueous solutions over the water-bath, whereas, on mixing an ethereal solution of picoline with an acid, nothing but a semi-fluid mass is precipitated, on account of the smallness of the quantity of water present. The solutions of picoline-salts decompose much less quickly on exposure to the air than the aniline-salts, assuming not a rose-red, but a brown colour. (Anderson.) The salts are thick, uncrystallisable liquids; they are inodorous, but taste like picoline, because that substance is set free by the alkali of the saliva. Those picoline-salts which contain a volatile acid evaporate without decomposition; those which contain the more fixed acids, give off a large quantity of picoline when their aqueous solutions are boiled, and leave syrupy acid salts which remain undecomposed till they are heated considerably above 100°, and then either give off their picoline undecomposed, or retain it mixed with fuscine. (Unverdorben.) — Picoline-salts are very soluble in water, and some of them are deliquescent. (Anderson.) The salts, even the tartrate, dissolve in all proportions in absolute alcohol. (Unverdorben.)

The compounds of picoline with *carbonic* and *boracic acid* are quickly decomposed by boiling with water; those with *phosphoric* acid are converted by boiling into acid salts. (Unverdorben.)

*Sulphite of Picoline.* — Picoline absorbs sulphurous acid gas, with strong fuming and considerable rise of temperature, and forms an oil which readily distils without decomposition, dissolves in water in all proportions, and is converted into sulphate of picoline on exposure to the air. (Unverdorben.)

*Sulphate of Picoline.* — *Biacid.* — When the colourless mixture of sulphuric acid with excess of picoline is evaporated over the water-bath, a large quantity of picoline escapes, and there remains a thick oil, which, on cooling, solidifies in a mass of transparent colourless plates. This mass, when exposed to the air, quickly deliquesces into a transparent colourless oil; it dissolves readily in alcohol, but does not crystallise from hot alcohol on cooling, and is insoluble in ether. (Anderson.) Anhydrous picoline mixes with oil of vitriol, the temperature of the mixture rising to ebullition, and forms a colourless oil which is insoluble in excess of picoline, and when boiled with water gives off picoline and is converted into an acid salt. (Unverdorben.)

| *Crystals.* | | | Anderson. |
|---|---|---|---|
| $C^{12}NH^7$ | 93 | 48·69 | |
| 2 $SO^3$ | 80 | 41·88 | 41·20 |
| 2 HO | 18 | 9·43 | |
| $C^{12}NH^7,2SO^3 + 2HO$ | 191 | 100·00 | |

[or rather $C^{12}NH^8O,HO,2SO^3$.]

*Hydriodate of Picoline.* — Picoline forms with iodine and water, in addition to other products (p. 267), a liquid which dissolves readily in water, alcohol and ether; is coloured brown from excess of iodine; and when evaporated with water, gives off picoline and hydriodate of picoline, and is converted into an acid salt. (Unverdorben.)

*Hydrochlorate of Picoline.* — The neutral mixture evaporated to a syrup over the water-bath, solidifies on cooling, in a mass of prisms, which when gently heated, sublime in transparent crystals deliquescing quickly on exposure to the air. (Anderson.) Dry hydrochlorate of picoline obtained by distilling its compound with chloride of copper, solidifies on cooling, in a very deliquescent, tallowy mass, having but little odour. By saturating picoline with hydrochloric acid gas, which process is attended with rise of temperature and production of fumes, a colourless oil is obtained, which volatilises with the watery vapour, and does not solidify even at — 25°.

*Nitrate of Picoline.* — Dilute nitric acid evaporated to dryness at a gentle heat with picoline, leaves a white crystalline mass which, at a stronger heat, sublimes in white feathery crystals. (Anderson.) — Nitrate of picoline when distilled, passes over, for the most part undecomposed, together with nitrate of picoline and a small quantity of ethereal oil, and, when the distillation is interrupted, leaves an extractive substance, and a resin soluble in potash, together with undecomposed nitrate of picoline.

Picoline forms double salts with *terchloride of antimony* and *bichloride of tin.* (Anderson.)

*Sulphate of Copper with Picoline.* — Sulphate of copper dissolves in anhydrous picoline, with separation of basic sulphate of copper, and forms a dark blue liquid, which, when exposed to the air, first gives off a portion of its picoline and dries up to a green mass, then gradually loses the whole of the picoline, and is converted into neutral sulphate of copper. From an aqueous solution of sulphate of copper also, picoline throws down only a portion of the copper in the form of a basic salt. — Picoline, whether anhydrous or dissolved in water, has no action upon oxide or carbonate of copper. (Unverdorben.)

*Chloride of Copper with Picoline.* — A solution of protochloride of copper is precipitated by excess of anhydrous picoline, and the brown crystalline precipitate recrystallised from boiling absolute alcohol, whereby it is obtained in yellowish brown four-sided tables. — They melt above 100°, being first converted, with partial evolution of anhydrous picoline, into a brownish yellow transparent liquid, which solidifies to a black viscid tar on cooling, and being finally resolved, with decomposition of the still remaining picoline, into hydrochlorate of picoline, together with a small quantity of gas and dichloride of copper. With potash, they give off perfectly pure picoline free from neutral oil. In contact with water or aqueous alcohol, they are resolved into picoline, hydrochlorate of picoline, and basic hydrochlorate of cupric oxide. They dissolve in 300 pts. of cold and 100 pts. of boiling absolute alcohol. (Unverdorben.)

*Protochloride of Copper* dissolves in anhydrous picoline, forming a beautiful blue solution; a concentrated aqueous solution also forms with it a clear blue mixture. (Unverdorben.)

*Chlorocuprate of Picoline.* — A solution of protochloride of copper in a small quantity of absolute alcohol, mixed with hydrochlorate of picoline (the picoline must be prepared from its compound with chloride of copper by the action of potash), and then with ether, amounting to $\frac{1}{3}$ of the mixture, yields yellowish crystalline laminæ, which must be washed with a mixture of equal parts of alcohol and ether. The laminæ melt when heated, giving off small quantities of water and picoline, and form a brownish yellow liquid, which on cooling solidifies in a yellow mass, but when further heated, yields hydrochlorate of picoline (which solidifies in a tallowy mass), and leaves dichloride of copper mixed with a small quantity of charcoal. They turn blue in the air, and give off picoline. They dissolve very readily in water, in 6 pts. of cold, and in a much smaller quantity of hot absolute alcohol. (Unverdorben.) — When aqueous protochloride of copper is evaporated with hydrochlorate of picoline, large rhombohedral crystals are obtained. (Anderson.)

*Chloride of Mercury with Picoline.* — Picoline immediately forms a curdy precipitate with a concentrated solution of corrosive sublimate, and separates silvery radiating needles after a while from a dilute solution. These needles give off picoline when dried by heat; also when boiled with water, a white powder being at the same time precipitated. They dissolve sparingly in cold, more readily in hot water, easily in dilute hydrochloric acid, forming a peculiar compound [doubtless the following], and in hot alcohol, crystallising therefrom in needles and feathers. (Anderson.) — Picoline added to aqueous corrosive sublimate throws down a white crystalline powder, which smells of picoline, dis-

solves in 10 pts. of boiling water, and also in warm alcohol and ether, crystallising out for the most part on cooling; when heated alone, it gives off, first picoline, then corrosive sublimate, and its aqueous solution when boiled, gives off picoline, and is converted into solution of corrosive sublimate; when heated with potash, it is resolved into picoline which escapes, mercuric oxide which is precipitated, and chloride of potassium. (Unverdorben.)

| | *Air-dried.* | | Anderson. |
|---|---|---|---|
| 12 C | 72·0 | 19·79 | 20·51 |
| N | 14·0 | 3·85 | |
| 7 H | 7·0 | 1·92 | 2·19 |
| 2 HgCl | 270·8 | 74·44 | |
| $C^{12}NH^7,2HgCl$ | 363·8 | 100·00 | |

*Chloromercurate of Picoline.* — Deposited as a transparent colourless oil permanent in the air, when an aqueous solution of corrosive sublimate is boiled down with hydrochlorate of picoline. (Unverdorben.)

Picoline does not precipitate nitrate of silver. (Anderson.)

*Chloride of Gold with Picoline.* — Picoline added to aqueous terchloride of gold throws down a lemon-yellow powder, which dissolves in a large quantity of boiling water, and crystallises therefrom in delicate yellow needles. — The yellow powder melts below 100°, forming a clear yellow glass, and when more strongly heated, gives off hydrochlorate of picoline, leaving gold together with a few other products of decomposition; it is slowly decomposed by boiling nitric acid; quickly by aqueous potash, yielding chloride of potassium, free picoline, and a precipitate of auric oxide; it is nearly insoluble in cold water, sparingly soluble in boiling water, and precipitates as a granular powder on cooling. (Unverdorben.)

*Chloroaurate of Picoline.* — Precipitated on mixing a solution of gold with hydrochlorate of picoline, in delicate yellow, inodorous crystals, which redden litmus. These crystals, when heated alone, melt, give off chlorine and hydrochlorate of picoline, and leave gold. With the smallest quantity of potash, they immediately give out the odour of picoline. They dissolve in 20 pts. of boiling water, and in hot aqueous sulphuric, hydrochloric or nitric acid, crystallising out again for the most part on cooling. They dissolve in alcohol more readily than in ether. (Unverdorben.)

*Chloride of Platinum with Picoline.* — Resembles the compound of chloride of gold with picoline; from a boiling aqueous solution it is precipitated as a powder on cooling. (Unverdorben.)

*Chloroplatinate of Picoline.* — A concentrated mixture of bichloride of platinum and hydrochlorate of picoline yields immediately, and a dilute mixture after 24 hours, orange-yellow needles, which may be purified from excess of picoline by recrystallisation from a hot solution of bichloride of platinum containing hydrochloric acid, and washing with alcohol and ether. — Orange-yellow slender needles, which dissolve in

about 4 pts. of boiling water, and readily also in alcohol. (Anderson.) — Yellow crystals soluble in 4 pts. of water. (Unverdorben.)

| | Dried at 100°. | | Anderson. | Wertheim (*from piperine*). |
|---|---|---|---|---|
| 12 C | 72·0 | 24·06 | 24·09 | 23·39 |
| N | 14·0 | 4·68 | | |
| 8 H | 8·0 | 2·68 | 3·05 | 2·94 |
| Pt | 99·0 | 33·09 | 32·53 | 32·63 |
| 3 Cl | 106·2 | 35·49 | | |
| $C^{12}NH^8Cl,PtCl^2$ | 299·2 | 100·00 | | |

¶. *Platinopicoline.* $C^{12}NH^5Pt = C^{12}NH^5Pt^2$. — Chloroplatinate of picoline is decomposed by boiling in the same manner as chloroplatinate of pyridine (x, 407), but more slowly, the decomposition not being complete till after 8 or 10 days; the addition of a small quantity of picoline, however, accelerates the action, causing it to be completed in a few hours. The product is the *bihydrochlorate of picoline* :

$$C^{12}NH^8Cl,PtCl^2 = C^{12}NH^5Pt,2HCl + HCl.$$

This salt is insoluble in water. It unites with chloroplatinate of picoline, forming the compound $C^{12}NH^5Pt,2HCl + C^{12}NH^8Cl, PtCl^2$, which crystallises in granules, but is much less soluble than the corresponding pyridine compound. (Anderson, *Ann. Pharm.* 96, 203.) ¶.

Picoline dissolves readily in *wood-spirit* (Anderson), *alcohol* and *ether* (Unverdorben.)

*Acetate of Picoline.* — May be distilled with water. (Unverdorben.)

*Cupro-Acetate of Picoline.* — The clear blue solution of cupric acetate in not too large a quantity of aqueous picoline, deposits, when exposed to the air, a basic salt in grass-green-crystals, which smell faintly of picoline, do not give off that base on exposure to the air, dissolve readily in water and alcohol, but are insoluble in ether; their aqueous solution when distilled, gives off, first picoline and then acetate of picoline, leaving acetate of copper with excess of oxide. — If the picoline is in excess in the blue solution, water and acetate of picoline volatilise, and rectangular prisms are formed which do not redden litmus, effloresce slowly in the air, dissolve readily in water and alcohol, but not in ether, and when boiled with water, decompose in the same manner as the green crystals. (Unverdorben.)

*Oxalate of Picoline.* — Aqueous oxalic acid mixed with excess of picoline and evaporated over lime, forms tufts of needles, and finally solidifies in a dense crystalline mass, which dissolves readily in water and in alcohol, either aqueous or absolute. It melts at 100°, giving off large quantities of picoline vapour, and leaves on cooling a thick liquid, which slowly deposits slender needles, probably consisting of the acid salt. (Anderson.)

*Butyrate of Picoline.* — Oil which may be distilled. (Unverdorben.)

Picoline mixes readily with *volatile oils* (Unverdorben), and with *fixed oils.* (Anderson.) It dissolves several *resins* which are separated therefrom by boiling with water. (Unverdorben.) With infusion of *gall-nuts* it forms a pale yellow curdy precipitate. With several kinds of extractive matter, it forms compounds which are not decomposed by boiling with water, but readily by potash. (Unverdorben.) It does not coagulate white of egg (Anderson); with equal quantities, coagulation takes place in a quarter of an hour. (Wertheim.)

## ¶. Ethylopicoline.

$$C^{16}NH^{11} = C^4H^4,C^{12}NH^7 = C^{12}N(C^4H^5,H^6).$$

ANDERSON. *Phil. Mag. J.* [4], 9, 214; *Ann. Pharm.* 94, 361.

Formed by the action of iodide of ethyl on picoline. When 1 vol. of anhydrous picoline is mixed with 2 vol. iodide of ethyl, and the mixture heated in a sealed tube placed in the water-bath, an action takes place attended with considerable evolution of heat, the liquid becoming turbid and separating into two layers, the upper of which solidifies in a crystalline mass of hydriodate of ethylopicoline. With the aid of heat, the action is complete in about ten minutes; it also takes place at ordinary temperatures, but then occupies several days. The hydriodate is recrystallised from a very small quantity of boiling alcohol and ether.

*Hydrated Oxide of Ethylopicoline* is obtained by treating the solution of the iodide with moist oxide of silver, and quickly separating the liquid from the resulting iodide of silver. If the action be too long continued, and especially if heat be applied, further decomposition takes place, and the liquid assumes a violet or crimson colour. — The filtered liquid is colourless; has a caustic taste and strong alkaline reaction; absorbs carbonic acid from the air; precipitates and redissolves alumina; precipitates corrosive sublimate; and exhibits generally with metallic salts the same reactions as potash or soda. When boiled, it assumes a deep red colour, and emits an odour of ethylamine, which base is more abundantly evolved on boiling the liquid with potash. The solution is partly decomposed by evaporation in vacuo, and leaves a hard gummy mass, which dissolves in water with blood-red colour. The formation of a fixed base by the action of oxide of silver on the hydriodate of ethylopicoline seems to show that picoline is a nitrile-base, like triethylamine, &c.

*Hydriodate* $C^{16}NH^{11},HI = C^{12}NH^7(C^4H^5),I$. — Crystallises from a mixture of alcohol and ether, in tabular crystals having a silvery lustre. Melts below 100°, forming an oily liquid. Dissolves very readily in water and alcohol, sparingly in ether. On treating the aqueous solution with a considerable quantity of potash, the hydriodate is deposited in the form of a thick oil, which gradually concretes into a crystalline mass. When boiled with strong potash, it gives off a volatile alkali.

| | | | Anderson. |
|---|---|---|---|
| 16 C | 96 | 38·70 | 38·57 |
| N | 14 | 5·67 | 5·61 |
| 12 H | 12 | 4·83 | 4·93 |
| I | 126 | 50·80 | 50·89 |
| $C^{16}NH^{12}I$ | 248 | 100·00 | 100·00 |

*Chloro-aurate.* — Prepared by decomposing the hydriodate with nitrate of silver, precipitating the excess of silver from the filtrate with hydrochloric acid, and adding a concentrated solution of terchloride of gold: the salt is then gradually deposited in golden-yellow flattened prisms, which dissolve sparingly in cold, readily in hot water; but are insoluble in alcohol and in ether.

| | | | Anderson. |
|---|---|---|---|
| 16 C | 96·0 | 20·83 | 20·59 |
| N | 14·0 | 3·06 | |
| 12 H | 12·0 | 2·60 | 2·75 |
| Au | 199·0 | 42·69 | 42·73 |
| 4 Cl | 141·6 | 30·82 | |
| $C^{16}NH^{12}Cl,AuCl^3$ | 462·6 | 100·00 | |

*Chloroplatinate.* — Prepared as the gold-salt. Separates gradually in orange-red tabular crystals. Dissolves readily in water, but is decomposed when its aqueous solution is boiled for some time.

| | | | | Anderson. | |
|---|---|---|---|---|---|
| 16 C | 96·0 | 29·33 | 29·15 | | |
| N | 14·0 | 4·31 | | | |
| 12 H | 12·0 | 3·66 | 3·76 | | |
| Pt | 99·0 | 30·16 | 29·75 | 29·78 | 29·91 |
| 3 Cl | 106·2 | 32·54 | | | |
| $C^{16}NH^{12}Cl,PtCl^2$ | 327·2 | 100·00 | | | |

*Alkaloïds resembling Picoline, but less volatile and less soluble in water.*

Discovered, together with picoline, in bone-oil, by Unverdorben in 1827, and prepared in the manner already described (pp. 265, 266). — [More recently, Anderson has discovered in bone-oil, two alkaloïds homologous with picoline, but less volatile, viz., *Lutidine* $C^{14}NH^9$, and *Collidine* $C^{16}NH^{11}$. The animine, olanine, and ammoline obtained by Unverdorben were probably mixtures of these two bases, in various proportions, and with other substances in addition.]

## 1. Animine.

Colourless oil, less volatile than picoline; its aqueous solution changes the colour of reddened litmus to violet.

Animine dissolves in 20 pts. of water. The solution becomes turbid when heated, and deposits animine, which redissolves on cooling.

With acids animine behaves like picoline and has about an equal degree of affinity for them.

With oil of vitriol it combines, with great rise of temperature, and forms an uncrystallisable oil, which, when boiled with water, gives off ammonia, and is converted into an acid salt, not further decomposible by concentration. This acid salt dissolves in any quantity of water or alcohol, and likewise in the peculiar ethereal oil contained in Dippel's oil, which is soluble in 65 per cent. alcohol.

Corrosive sublimate forms with hydrochlorate of animine, a colourless, oily, neutral double salt; on mixing animine with excess of hot aqueous corrosive sublimate, a compound of mercuric chloride with animine separates in the form of a yellowish oil, which becomes hard and brittle on cooling, and when boiled for some time with water, is resolved into animine which volatilises, and corrosive sublimate which remains dissolved.

With gold-solution, hydrochlorate of animine forms a brownish-yellow, oily double salt; and with platinum-solution, a crystallisable double salt sparingly soluble in water.

Benzoate of animine is oily, sparingly soluble in cold, more readily in boiling water, and on account of the inferior volatility of animine, is less easily decomposed by boiling with water than benzoate of picoline.

Animine dissolves in all proportions, in alcohol, ether, and oils. A mixture of animine and picoline slowly dissolves copal; and when the somewhat thickened solution is boiled in a retort with alcohol of 30 per cent., the whole of the picoline passes quickly over, together with a small quantity of animine, and leaves in the alcoholic water, a light-coloured oil, which is a compound of copal with pure animine. This compound is easily decomposed by potash; gives up only part of its animine to aqueous acids; but if it be previously dissolved in alcohol of 65 per cent., hydrochloric acid precipitates the whole of the copal, and pure hydrochlorate of animine remains in solution. (Unverdorben, *Pogg.* 11, 59 and 67).

## 2. Olanine.

Colourless oil, heavier than water; smells like animine, but less strongly, also like aniline, not unpleasantly; blues litmus but very feebly.

Slowly turns brown on exposure to the air, a small quantity of fuscine being formed at the same time.

Olanine is but very slightly soluble in water. It decomposes the same metallic salts as picoline, and combines with acids, forming salts resembling those of picoline, but not crystallisable; they are decomposed by the same bodies as the picoline-salts.

Hydrochlorate of olanine forms with hydrochlorate of ferric oxide, a dark brown, oily double salt, which is not decomposible by acids; and dissolves readily in 2 parts of cold water, but requires 4 pts. of boiling water to dissolve it; so that the cold solution when heated, deposits an oil which redissolves on cooling; it likewise dissolves in oil of cummin, forming a solution which is not decomposed by boiling.

Hydrochlorate of olanine behaves with corrosive sublimate like hydrochlorate of animine. — When an aqueous solution of corrosive sublimate is mixed with pure olanine, a yellow resinous precipitate is formed, which is not decomposed by boiling with water (thereby affording a distinction between olanine and animine), dissolves in 1000 pts. of boiling water, whence it is precipitated in the crystalline state on cooling, but is insoluble in alcohol (also a distinction between olanine and animine).

With hydrochlorate of auric oxide, hydrochlorate of olanine forms a yellowish-brown, oily double salt, which is heavier than water, not decomposible by acids; deposits a small quantity of gold when boiled for some time with water; dissolves sparingly in cold, more freely in boiling water, and in any quantity of alcohol or ether. — Free olanine forms with

hydrochlorate of auric oxide, a brown, hard, basic double salt, which is soluble in alcohol, insoluble in water, and is transformed, very slowly by boiling with hydrochloric acid, but very easily on addition of alcohol, into the oily neutral double salt. With hydrochlorate of platinic oxide, olanine forms a tarry double salt, which dissolves readily in water and alcohol, but not in ether.

Olanine dissolves easily and in all proportions in alcohol and ether. (Unverdorben, *Pogg.* 11, 59.)

## 3. Ammoline.

Colourless oil, heavier than water, boiling at a point very near that of the fixed oils, and consequently distilling over but sparingly with water; blues litmus very strongly.

By chlorine, it is completely resolved into hydrochlorate of ammonia, animine, fuscine, and an extractive matter.

Ammoline dissolves in about 200 pts. of cold and 40 pts. of boiling water; the solution may be concentrated by boiling without much loss.

At the boiling heat, it expels ammonia from the aqueous sulphate and hydrochlorate; forms with acids, uncrystallisable salts, which yield but little ammoline when boiled with ammonia.

The borate, sulphate, hydrochlorate, nitrate, acetate and succinate of ammoline are not crystallisable; they dissolve in any quantity of water or alcohol, but are insoluble in ether. — The hydrochlorate and acetate of ammoline may be distilled almost without decomposition. — The nitrate decomposes when heated, in such a manner that part of the ammoline is destroyed, and the rest passes over in the free state. — With heavy metallic salts, ammoline forms double salts similar to those of olanine.

Ammoline mixes in all proportions with alcohol and ether, and combines very intimately with many resins and extractive matters. (Unverdorben, *Pogg.* 11, 74.)

*Azotiodine-nucleus* $C^{12}NIH^4$.

## Iodaniline.

$C^{12}NH^6I = C^{12}NIH^4,H^2$.

A. W. Hofmann. (1848.) *Ann. Pharm.* 67, 64; *Chem. Soc. Qu. J.* 1, 271.

*Formation.* By the action of iodine or iodide of cyanogen on aniline (pp. 251, 253).

*Preparation.* $1\frac{1}{2}$ pt. of iodine is gradually dissolved in 1 pt. of aniline; the solution mixed with hydrochloric acid of sp. gr. 1·11 (a stronger acid would separate part of the hydrochlorate of aniline); the solution of hydrochlorate of aniline, hydriodic acid, &c., separated by

filtration from the precipitated and still strongly coloured hydrochlorate of iodaniline, which is sparingly soluble in water; the precipitate washed several times with hydrochloric acid, and crystallised several times from boiling water, at last after boiling with animal charcoal, till the crystals, which are at first ruby-coloured and contain free iodine, together with a brown induretted decomposition-product of aniline, are completely decolorised; and the iodaniline precipitated from their aqueous solution by ammonia, as a white crystalline powder, which—in order to free it from any of the yellowish decomposition-product and phosphate of lime from the animal charcoal, that may still adhere to it—is dissolved in alcohol, filtered from the yellowish product, and precipitated by water in the form of a white crystalline mass. — The liquid filtered therefrom yields by evaporation yellowish oily drops which crystallise on cooling.

*Properties.* White crystalline powder, which crystallises from the solutions in prisms and needles, never in octohedrons; the mass solidified from cooling also never exhibits the cleavage-faces of the octohedron. Heavier than water. Melts at 60°, forming a yellowish oil, and at the moment of solidification, shows a temperature of 51°, but sometimes remains liquid even at the ordinary temperature, in which case, contact with a glass rod often causes it to solidify suddenly in a crystalline mass. When evaporated at a rather strong heat, it volatilises undecomposed, and easily distils over even with vapour of water. Has a vinous odour and a burning aromatic taste. Has no action on vegetable colours. Like aniline, it imparts a deep yellow colour to firwood and elder-pith; but chloride of lime colours it, not violet but reddish.

| | | | Hofmann. |
|---|---|---|---|
| 12 C | 72 | 33·03 | 33·08 |
| N | 14 | 6·42 | |
| 6 H | 6 | 2·75 | 2·83 |
| I | 126 | 57·80 | 57·87 |
| $C^{12}NH^6I$ | 218 | 100·00 | |

*Decompositions.* 1. The vapour *burns* with a bright sooty flame. — 2. In contact with the *air*, iodaniline becomes quickly covered with a brown, metallically lustrous film, and gradually assumes a black colour extending throughout the whole mass. — 3. *Chlorine* decomposes iodaniline into terchloraniline, terchlorocarbolic acid (as with aniline, p. 250), and chloride of iodine. — 4. With *bromine*, alcoholic iodaniline solidifies in the form of crystalline terbromaniline, while all the iodine is set free as bromide of iodine. — 5. *Chlorate of potash* with hydrochloric acid forms, as with aniline, terchlorocarbolic acid and chloranil. — 6. With strong boiling nitric acid, iodaniline forms, with brisk action and evolution of iodine-vapour, a solution from which picric acid crystallises on cooling. — 7. Crystallised *chromic acid* decomposes iodaniline with violence, but does not set it on fire. — 8. Gently heated *potassium* decomposes iodaniline with violence, forming iodide and cyanide of potassium. — Potassium-amalgam introduced into aqueous nitrate of iodaniline, immediately forms iodide of potassium, and reproduces a small quantity of aniline, whilst the greater portion is converted into a yellow crystalline substance having an aromatic odour. *Zinc* immersed in iodaniline supersatured with sulphuric acid, eliminates iodine and aniline, so that after a few minutes the liquid

forms a blue colour with starch, and after saturation with potash, gives up aniline to ether. — 9. When chloride of cyanogen is passed through iodaniline dissolved in ether, hydrochlorate of iodaniline is first precipitated but afterwards disappears, and the iodaniline is converted into a transparent, slowly crystallising resin, which is a mixture of hydrochlorate of biniodomelaniline and iodaniline-urea. Formation of hydrochlorate of biniodomelaniline:

$$2C^{12}NH^{6}I + C^{2}NCl = C^{26}N^{3}H^{11}I^{2},HCl;$$

Formation of iodaniline-urea and hydrochlorate of iodaniline:

$$2C^{12}NH^{6}I + C^{2}NCl + 2HO = C^{14}N^{2}H^{7}IO^{2} + C^{12}NH^{6}I,HCl.$$

*Combinations.* Iodaniline dissolves very sparingly in cold *water*, and crystallises from boiling water in interlaced hairs.

It dissolves in *bisulphide of carbon.*

Iodaniline is a weaker base than aniline, and is therefore precipitated by aniline, and precipitates only alumina, not oxide of zinc or sesquioxide of iron. The *Salts of Iodaniline* crystallise as readily as the aniline-salts, and are generally less soluble.

*Sulphate of Iodaniline.* — White shining scales, containing 19·24 p. c. $HO,SO^{3}$, and therefore = $C^{12}NH^{6}I,HO,SO^{3}$; sparingly soluble in cold, more soluble in hot water; the solution when boiled deposits a product insoluble in boiling water.

*Hydriodate of Iodaniline.* — Radiated crystalline mass, easily soluble in water and quickly decomposing.

*Hydrobromate of Iodaniline.* — Very much like the hydrochlorate.

*Hydrochlorate of Iodaniline.* — Crystallises from boiling water in nacreous laminæ and thin needles. Contains 14·44 p. c. hydrochloric acid. Dissolves sparingly in cold water, and is precipitated therefrom almost entirely by strong hydrochloric acid; dissolves in alcohol but not in ether.

*Nitrate of Iodaniline.* — Crystallises from hot water in long capillary needles. The salt does not precipitate silver-solution; it dissolves both in cold and in hot water better than the other salts of iodaniline, and readily also in alcohol and ether.

Iodaniline forms with *sulphate of copper* a yellowish precipitate, probably a double compound.

With *terchloride of gold,* hydrochlorate of aniline forms a scarlet precipitate, which quickly decomposes.

*Chloroplatinate of Iodaniline.* — The orange-yellow crystalline precipitate formed by hydrochlorate of iodaniline in bichloride of platinum, is easily purified by washing with ether.

| | | | Hofmann. |
|---|---|---|---|
| 12 C | 72·0 | 16·97 | 16·82 |
| N | 14·0 | 3·30 | |
| 7 H | 7·0 | 1·65 | 1·87 |
| I | 126·0 | 29·70 | |
| Pt | 99·0 | 23·34 | 23·14 |
| 3 Cl | 106·2 | 25·04 | |
| $C^{12}NH^{7}ICl,PtCl^{2}$ | 424·2 | 100·00 | |

*Oxalate of Iodaniline.* — Long flat needles containing 17·39 p. c. $C^4H^2O^8$, and therefore $= 2C^{12}NH^6I,C^4H^2O^8$. They dissolve sparingly in water and alcohol, but are insoluble in ether.

Iodaniline dissolves in *wood-spirit, alcohol, ether, acetone,* and in *oils* both *fixed* and *volatile.* (Hofmann.)

### *Azobromine-nucleus* $C^{12}NBrH^4$.

## Bromaniline.

$$C^{12}NBrH^6 = C^{12}NBr^4,H^2.$$

HOFMANN. (1845.) *Ann. Pharm.* 53, 42.

*Formation.* By heating bromisatine with potash.

*Preparation.* Bromisatine is distilled with strong potash-ley till the residue is nearly dry, and gives off, together with ammonia, a brown oil which no longer solidifies; and the oily drops which passed over at the beginning of the distillation, and have solidified in the crystalline form, are washed with water on a filter, and recrystallised from boiling alcohol.

*Properties.* Colourless, regular octohedrons, exactly like chloraniline, melting at 50° into a violet oil, which in solidifying sinks to the temperature of 46°; in odour and taste it resembles chloraniline.

| | | | Hofmann. |
|---|---|---|---|
| 12 C | 72 | 41·86 | 42·45 |
| N | 14 | 8·14 | |
| 6 H | 6 | 3·49 | 3·75 |
| Br | 80 | 46·51 | |
| $C^{12}NH^6Br$ | 172 | 100·00 | |

Bromaniline is easily reduced to aniline by potassium-amalgam (*Ann. Pharm.* 67, 76). — With excess of bromide of ethyl, it is quickly converted into hydrobromate of ethylobromaniline;

$$C^{12}NBrH^6 + C^4H^5Br = C^{16}NBrH^{10},HBr.$$

Its aqueous solution imparts a violet colour to aqueous chloride of lime, weaker than that produced by aniline, but stronger than that produced by chloraniline. Its salts colour chloride of lime red-brown and firwood yellow. Bromaniline dissolves readily in bisulphide of carbon.

*Hydrochlorate of Bromaniline.* — Crystallises from boiling water in nacreous radiated fibres, but, by evaporation over oil of vitriol, in well formed prisms belonging to the oblique prismatic system. May be derived from *fig.* 81; $a : a = 128° 35'$; $u : u$ behind $= 80° 27'$. (Müller.) They contain 17·71 p. c. hydrochloric acid, and are therefore $C^{12}NH^6Br,HCl$.

*Chloroplatinate of Bromaniline.* — Precipitated on mixing hydrochlorate of bromaniline with bichloride of platinum; closely resembles the corresponding compound of chloraniline; contains 26·19 p. c. platinum, and is therefore $C^{12}NH^6Br,HCl + PtCl^2$.

*Oxalate of Bromaniline.* — The crystalline powder precipitated from alcoholic bromaniline by aqueous oxalic acid, is collected on a filter and crystallised from boiling water. Indistinct crystals, sparingly soluble in water and alcohol. (Hofmann.)

| *Air-dried crystals.* | | | Hofmann. |
|---|---|---|---|
| 28 C | 168 | 38·71 | 38·93 |
| 2 N | 28 | 6·45 | |
| 14 H | 14 | 3·23 | 3·34 |
| 2 Br | 160 | 36·86 | |
| 8 O | 64 | 14·75 | |
| $2C^{12}NH^6Br,C^4H^2O^8$ | 434 | 100·00 | |

*Azobromine-nucleus* $C^{12}NBr^2H^3$.

## Bibromaniline.

$$C^{12}NBr^2H^5 = C^{12}NBr^2H^3,H^2.$$

Hofmann. (1845.) *Ann. Pharm.* 53, 47.

*Preparation.* Bibromisatine is distilled with hydrate of potash, the distilled and crystallised oil freed from ammonia by washing with water, and crystallised from boiling alcohol.

*Properties.* Large, flat, somewhat rhombic prisms, melting between 50° and 60°, into a dark-coloured oil, which often remains liquid long after cooling, but then crystallises suddenly on agitation.

| | | | Hofmann. |
|---|---|---|---|
| 12 C | 72 | 28·68 | 28·77 |
| N | 14 | 5·58 | |
| 5 H | 5 | 1·99 | 2·40 |
| 2 Br | 160 | 63·75 | |
| $C^{12}NH^5Br^2$ | 251 | 100·00 | |

Bibromaniline dissolves sparingly in boiling *water*, forming a liquid which becomes turbid on cooling and gradually deposits slender needles.

It is a very weak base; its solution in *acids* colours firwood yellow; it is precipitated by alkalis. It forms crystallisable salts, which however are less stable than those of bromaniline.

The solution of bibromaniline in boiling *hydrochloric acid*, yields on cooling, laminæ containing 13·31 p. c. hydrochloric acid; when they are dissolved in water, part of the base separates in thin oily drops; and the solution evaporated under a bell-jar over lime, which abstracts the greater

part of the hydrochloric acid, deposits nearly pure crystalline bibromaniline.

The hydrochloric acid solution forms a crystalline orange-yellow precipitate with *bichloride of platinum.*

Bibromaniline is soluble in *alcohol.* (Hofmann.)

### *Azobromine-nucleus* $C^{12}NBr^3H^2$.

## Terbromaniline.

$$C^{12}NBr^3H^4 = C^{12}NBr^3H^2,H^2.$$

FRITZSCHE. (1842.) *J. pr. Chem.* 28, 204.
A. W. HOFMANN. *Ann. Pharm.* 53, 50.

*Bromaniloïd* (Fritsche).

*Preparation.* 1. Dry bromine is mixed with aniline in such proportion that the mixture solidifies completely after a while in the crystalline form, after which alcohol is added, and also more bromine till its odour becomes permanent. The greenish-grey crystalline magma of tolerably pure terbromaniline is then separated by filtration from the greenish-yellow alcoholic liquid, which contains hydrobromic acid and the decomposition-products of the alcohol, and deposits more terbromaniline when mixed with water; after which it is washed on the filter with alcohol, and dissolved in hot alcohol: the solution thus obtained yields nearly colourless crystals. (Fritzsche.) — 2. The aqueous solution of an aniline-salt is mixed with aqueous bromine, which disappears and produces a white turbidity and precipitation of microscopic needles, the addition of bromine being continued till the precipitation ceases and a slight odour of bromine remains; the precipitated powder, which has a reddish tint arising from a decomposition-product, collected, and freed from this impurity by distillation in a small retort; and the distillate, which solidifies in a crystalline mass, recrystallised from boiling alcohol. (Fritzsche.) — 3. An aqueous solution of hydrochlorate of bromaniline is mixed with aqueous bromine, the violet-white precipitate distilled with water, whereby snow-white crystals are obtained at first, but afterwards violet crystals which cannot be decolorised by recrystallisation from alcohol. (Hofmann.)

*Properties.* Crystallised from hot alcohol, it forms colourless, shining, long, slender needles; but when solidified after fusion, it is of a crystalline texture, brittle and easily pulverised. Melts at 117° into a clear liquid; boils at about 300°; distils over unchanged (Fritzsche); and sublimes in radiating crystals having a silky lustre. (Hofmann.)

| | | | Fritzsche. | Hofmann (*coloured.*) |
|---|---|---|---|---|
| 12 C | 72 | 21·82 | 22·05 | 23·16 |
| N | 14 | 4·24 | 4·72 | |
| 4 H | 4 | 1·21 | 1·21 | 1·51 |
| 3 Br | 240 | 72·73 | 71·80 | |
| $C^{12}NH^4Br^3$ | 330 | 100·00 | 99·78 | |

*Decompositions.* 1. Strong boiling *nitric acid* decomposes terbromaniline. — 2. Warm *oil of vitriol* dissolves it without decomposition, acquiring a purple colour from decomposition only when heated nearly to the boiling point. Strong boiling potash-ley has no action upon it. (Fritzsche.)

*Combinations.* Insoluble in water. (Fritzsche.)

Terbromaniline dissolves abundantly in warm *oil of vitriol*, separating uncombined on cooling, and is precipitated in the crystalline state by water. (Fritzsche.)

It is not basic, and does not dissolve either in dilute acids or in alkalis. (Fritzsche, Hofmann.)

It dissolves sparingly in cold, readily in *boiling alcohol* and in *ether*. (Fritzsche.)

*Azochlorine-nucleus* $C^{12}NClH^4$.

## Chloraniline.

$C^{12}NClH^6 = C^{12}NClH^4,H^2$.

A. W. Hofmann. (1845.) *Ann. Pharm.* 53, 1.

*Preparation.* Chlorisatine is distilled with potash-ley or hydrate of potash, till the residue has become solid, gives off ammonia together with the hydrogen, and yields a blue sublimate and a brown oil which no longer solidifies on cooling. The solidified oil which first passed over is then collected on a filter, freed from ammonia by water, and crystallised from boiling alcohol.

*Properties.* Octohedrons having a diamond lustre, heavier than water, melting between 64° and 65°, into a yellow oil which solidifies at 57° in large octohedrons. Evaporates even at ordinary temperatures, so that hydrochloric acid held over it produces fumes; may be easily distilled with water; boils by itself at a temperature above 200°, and with some decomposition, so that, together with the oil, the above-mentioned blue product passes over. Has an agreeable vinous odour and an aromatic burning taste like that of aniline. Does not act upon red litmus or turmeric, but turns dahlia flowers green.

| *Air-dried crystals.* | | | Hofmann. |
|---|---|---|---|
| 12 C | 72·0 | 56·51 | 56·19 |
| N | 14·0 | 10·99 | 11·38 |
| 6 H | 6·0 | 4·71 | 5·02 |
| Cl | 35·4 | 27·79 | 27·45 |
| $C^{12}NClH^6$ | 127·4 | 100·00 | 100·04 |

*Decompositions.* 1. Chloraniline *burns* with a bright, strongly fuliginous flame, having a bright green border. — 2. *Chlorine* together

with water, converts chloraniline, partly into terchloraniline, partly into terchlorocarbolic acid:

$$C^{12}NClH^6 + 4Cl = C^{12}NCl^3H^4 + 2HCl;$$

and:

$$C^{12}NClH^6 + 4Cl + 2HO = C^{12}Cl^3H^3O^2 + HCl + NH^4Cl.$$

3. *Bromine*, either anhydrous or hydrated, decomposes chloraniline, with great evolution of heat, forming bibromochloraniline and hydrobromic acid:

$$C^{12}NClH^6 + 4Br = C^{12}NClBr^2H^4 + 2HBr.$$

4. Heated with strong *nitric acid*, it begins to boil and continues boiling even after removal from the fire; gives off nitrous acid; and yields, first, a dark red, then a black opaque liquid, and afterwards, as the heating is continued, a clear scarlet solution, which does not precipitate nitrate of silver, and on cooling, yields, sometimes golden-yellow needles resembling picric acid, and probably consisting of binitrochlorocarbolic acid $C^{12}X^2ClH^3,O^2$, sometimes a resin, which is precipitated by water in yellow flakes, and dissolves with deep yellow colour in alkalis, alcohol and ether; the solution of this resin in alkalis is precipitated by acids, and its ammoniacal solution, when freed from excess of ammonia by boiling, precipitates silver solution reddish yellow, sometimes also in yellow crystalline spangles. — 5. The aqueous solution of chloraniline acquires a very faint violet tint when treated with *chloride of lime*. — 6. With *chlorate of potash* and *hydrochloric acid*, chloraniline forms a violet-red, then a turbid brown, and ultimately a colourless liquid, which at first deposits crystallising chloranil, together with ter- or quintochlorocarbolic acid, in the form of a brown viscid substance soluble in alcohol, but after decoloration contains nothing but chloranil and sal-ammoniac; the same reaction therefore as with aniline:

$$C^{12}NClH^6 + 4Cl + 2HO = \underbrace{C^{12}Cl^3H^3O^2}_{\text{terchlorocarbolic acid.}} + NH^4Cl + HCl;$$

further:

$$C^{12}NClH^6 + 8Cl + 2HO = \underbrace{C^{12}Cl^5HO^2}_{\text{quintochloro-carbolic acid.}} + NH^4Cl + 3HCl;$$

and:

$$C^{12}NClH^6 + 6Cl + 4O = \underbrace{C^{12}Cl^4O^4}_{\text{chloranil.}} + NH^4Cl + 2HCl.$$

7. The crystals, immersed in aqueous *chromic acid* turn brown and become resinised; the dry mixture takes fire at the melting point of chloraniline. — 8. Aqueous chloraniline imparts to *ferric salts* a green colour by deoxidation, and on boiling, deposits a blackish violet product soluble in alcohol. — 9. When the vapour is passed over lime at a low red heat, aniline and ammonia pass over, a large quantity of charcoal is separated, and chloride of calcium is formed:

$$2C^{12}NClH^6 + 2CaO = C^{12}NH^7 + C^{12} + 2CaCl + NH^3 + 2HO.$$

10. Melted *potassium* immersed in the vapour of chloraniline, forms chloride and cyanide of potassium, with vivid incandescence and separation of a large quantity of charcoal. On the other hand, *potassium-amalgam*, with water, reduces chloraniline to aniline. (*Ann. Pharm.* 67, 76.)

*Combinations.* — Chloraniline dissolves sparingly in *water;* the boiling solution becomes milky on cooling and deposits octohedrons.

It dissolves readily in *bisulphide of carbon.*

Chloraniline is not so strong a base as aniline; it does not precipitate sulphate of alumina or the salts of ferric oxide, ferrous oxide or zinc-oxide; it expels ammonia from ammoniacal-salts when heated with them, but is itself precipitated by ammonia from its hydrochloric acid solution, and neutralises acids but imperfectly. The *Salts of Chloraniline* mostly crystallise readily, and, in consequence of their sparing solubility, are generally precipitated on mixing an acid with alcoholic chloraniline, in the form of a crystalline pulp, which may be purified by recrystallisation from boiling water or alcohol. They are mostly colourless or yellowish in mass, and violet when they contain excess of acid; they redden litmus even when completely saturated with the base. Like the aniline-salts, they impart a deep yellow colour to firwood and elder-pith, but with chloride of lime, they assume only a very faint violet tint, changing afterwards to orange-yellow. They are immediately decomposed by alkalis; also by alkaline carbonates, with evolution of carbonic acid, inasmuch as that acid does not combine with chloraniline.

*Phosphate of Chloraniline.* — Alcoholic chloraniline solidifies with aqueous phosphoric acid into a magma of crystalline laminæ, which dissolve pretty readily in water and alcohol.

*Sulphate of Chloraniline.* — The white crystalline magma, into which alcoholic chloraniline solidifies when mixed with a small quantity of acid, yields, when dissolved in boiling water, confused violet-white laminæ, and when dissolved in boiling alcohol, silvery needles arranged in stellate groups. The crystals when heated give off a small quantity of chloraniline, then blacken, and evolve sulphurous acid. They are less soluble in alcohol than in water.

| | *Crystals.* | | Hofmann. |
|---|---|---|---|
| 12 C | 72·0 | | 40·82 |
| 7 H | 7·0 | | 3·97 |
| NClO | 57·4 | | 32·55 |
| $SO^3$ | 40·0 | | 22·66 |
| $C^{12}NClH^6,HO,SO^3$ | 176·4 | | 100·00 |

*Hydrochlorate of Chloraniline.* — Hydrochloric acid saturated at a boiling heat with chloraniline, yields on cooling large crystals, which may be still further developed by slow evaporation of their aqueous solution over oil of vitriol. They have the same form as hydrochlorate of bromaniline (p. 278), $a : a = 127° \ 48'$. They contain 22·1 per cent. of hydrochloric acid. They are permanent in the air, become opaque when

heated, and sublime undecomposed when cautiously heated, whereas sudden heating decomposes them, with formation of a violet vapour.

*Nitrate of Chloraniline.* — The solution of chloraniline in warm dilute nitric acid becomes filled, as it cools, with large crystalline laminæ, mostly of a reddish colour. These crystals, which cannot be sublimed without decomposition, melt when heated in a tube, into a dark-coloured mass, which dissolves with splendid violet colour in alcohol, while part of the salt crystallises out undecomposed. The salt dissolves pretty readily in water and alcohol.

A mixture of the aqueous solutions of chloraniline and *protochloride of tin* soon solidifies into a silver-shining crystalline mass.

Aqueous *sulphate of copper*, which is not precipitated by aqueous chloraniline, soon becomes decolorised by boiling with crystalline chloraniline, and deposits a bronze-coloured crystalline mass, which is insoluble in water, and dissolves but sparingly in boiling alcohol, whence it crystallises in spangles on cooling.

The cold aqueous mixture of chloraniline and *corrosive sublimate* immediately forms a white precipitate, but the hot mixture remains clear at first, but then quickly becomes turbid, and solidifies into a magma of needle-shaped crystals of the double salt.

Aqueous chloraniline forms a red-brown precipitate with *terchloride of gold.*

*Chloraplatinate of Chloraniline.* — A cold solution of hydrochlorate of chloraniline forms with bichloride of platinum, a beautiful orange-coloured precipitate, and a hot mixture solidifies on cooling into a magma composed of white crystalline laminæ. These, when washed with a small quantity of water, and then dissolved in a larger quantity, are deposited, by evaporation over oil of vitriol, in crystalline nodules which redden litmus, become covered with a violet film on exposure to light, and dissolve readily in water and alcohol, especially at a boiling heat.

| | | | Hofmann. |
|---|---|---|---|
| 12 C | 72·0 | 21·58 | 22·03 |
| N | 14·0 | 4·20 | |
| 7 H | 7·0 | 2·10 | 2·30 |
| Pt | 99·0 | 29·68 | 29·34 |
| 4 Cl | 141·6 | 42·44 | |
| $C^{12}NClH^6,HCl + PtCl^2$ | 333·6 | 100·00 | |

Aqueous chloraniline forms an orange-coloured precipitate with *chloride of palladium.*

Chloraniline dissolves in *wood-spirit, alcohol* (readily when hot), in *ether*, (which abstracts it from the aqueous solution,) and in *acetone.*

*Oxalate of Chloraniline.* — The solution of chloraniline in the warm aqueous acid yields on cooling, crystals, which when recrystallised from boiling water, form prisms made up of smaller ones joined together. They have a sweetish burning taste, and dissolve sparingly in water and alcohol; the aqueous solution becomes coloured on exposure to the air and deposits a red powder.—It does not appear possible to obtain a bibasic salt in the crystalline state.

| | Crystals. | | | | | Hofmann. |
|---|---|---|---|---|---|---|
| 16 C | 96·0 | .... | 42·40 | ........ | 42·59 |
| NCl | 49·4 | .... | 21·82 | | |
| 9 H | 9·0 | .... | 3·98 | ........ | 4·24 |
| 9 O | 72·0 | .... | 31·80 | | |
| $C^{12}NClH^6,HO,C^4H^2O^8$ | 226·4 | .... | 100·00 | | |

The hot-saturated aqueous solution of chloraniline mixed with *tincture of galls*, forms yellow flakes on cooling. — Chloraniline dissolves in *oils*, both *fixed* and *volatile*.

*Azochlorine-nucleus* $C^{12}NCl^2H^3$.

## Bichloraniline.

$C^{12}NCl^2H^5 = C^{12}NCl^2H^3,H^2$.

Hofmann. (1845.) *Ann. Pharm.* 53, 33 and 57.

By distilling bichlorisatine, still containing chlorisatine, with hydrate of potash, long prisms are obtained consisting of bichloraniline with a little chloraniline. (Hofmann.)

*Azochlorine-nucleus* $C^{12}NCl^3H^2$.

## Terchloraniline.

$C^{12}NCl^3H^4 = C^{12}NCl^3H^2,H^2$.

Erdmann. (1840.) *J. pr. Chem.* 19, 331; 25, 472.
Hofmann. *Ann. Pharm.* 53, 35.

The *Chlorindatmit* of Erdmann, who however overlooked the nitrogen contained in it.

*Preparation.* 1. Distils over in the preparation of terchlorocarbolic acid (pp. 182, 3). — 2. In the action of chlorine upon aniline or chloraniline, there is formed a mixture of terchloraniline and terchlorocarbolic acid (pp. 250, 282); and when this mixture is distilled with potash-ley into a well-cooled receiver, the terchloraniline passes over in needles floating on the water, and an oil which solidifies in the crystalline form.

*Properties.* Delicate, white, very fragile needles and laminæ, easily melting into a colourless oil which crystallises on cooling; has a peculiar odour; volatile. Neutral. (Erdmann, Hofmann.)

| | | | | Hofmann. | Erdmann. |
|---|---|---|---|---|---|
| 12 C | 72·0 | .... | 36·70 | 37·65 | 36·89 |
| N | 14·0 | .... | 7·13 | | |
| 3 Cl | 106·2 | .... | 54·13 | | 53·58 |
| 4 H | 4·0 | .... | 2·04 | 2·44 | 2·23 |
| $C^{12}NCl^3H^4$ | 196·2 | .... | 100·00 | | |

*Decompositions.* — 1. With *nitric acid* it evolves nitrous fumes and forms a yellow solution which turns red when mixed with potash. (Erdmann.) — 2. The vapour passed over heated soda-lime, yields a large quantity of ammonia, and when passed over melted potassium, it yields a large quantity of cyanide of potassium. (Hofmann.) — Not decomposed by distillation with potash-ley. (Erdmann, Hofmann.)

*Combinations.* Dissolves sparingly in cold, more freely in boiling *water.* (Hofmann.)

Does not combine either with *acids* or with *alkalis.*

Dissolves readily in *alcohol* and *ether.* (Hofmann.)

### *Azochlorobromine-nucleus* $C^{12}NClBr^2H^2$.

## Chlorobibromaniline.

$$C^{12}NClBr^2H^4 = C^{12}NClBr^2H^2,H^2.$$

HOFMANN. (1845.) *Ann. Pharm.* 53, 38.

*Preparation.* 1. Crystalline chloraniline treated with anhydrous bromine becomes very hot and gives off a large quantity of hydrobromic acid, assumes a violet colour, and is converted, after it no longer absorbs bromine even when melted, into chlorobibromaniline, which solidifies on cooling, and must be washed with cold water and recrystallised from alcohol. — 2. When the whitish precipitate which bromine-water forms in an aqueous solution of a salt of chloraniline, is dissolved in hot alcohol, a pale violet solution is obtained which yields needle-shaped crystals.

*Properties.* White prisms, often with a tinge of red. They melt in hot water, forming a brown oil, which volatilises with the vapour of boiling water and sublimes in shining needles.

| | | | | Hofmann. |
|---|---|---|---|---|
| 12 C | 72·0 | .... | 25·23 | 25·43 |
| N | 14·0 | .... | 4·91 | |
| Cl | 35·4 | .... | 12·40 | |
| 2 Br | 160·0 | .... | 56·06 | |
| 4 H | 4·0 | .... | 1·40 | 1·52 |
| $C^{12}NClBr^2H^4$ | 285·4 | .... | 100·00 | |

It is decomposed by strong nitric acid.

It is insoluble in water.

It does not exhibit the characters of a salifiable base; dissolves indeed, with violet colour, in *oil of vitriol*, but is precipitated therefrom by water; dissolves also in hot strong *hydrochloric acid*, but the greater part of it separates on cooling, and the rest on addition of water.

It dissolves without alteration in warm *ammonia* and *potash*.

Does not form compounds with chloride of mercury or bichloride of platinum.

Dissolves in *alcohol* and *ether*. (Hofmann.)

¶. *Azonitroso-nucleus* $C^{12}N(NO^2)H^4$.

## Nitrosaniline.

$$C^{12}N^2H^6O^2 = C^{12}N(NO^2)H^4,H^2.$$

A. H. Church & W. H. Perkin. *Chem. Soc. Qu. J.* 9, 1.

*Formation and Preparation.* By the action of nascent hydrogen on binitrobenzene:

$$C^{12}N^2H^4O^8 + 8H = C^{12}N^2H^6O^2 + 6HO.$$

Pure zinc in the form of a long strip is introduced into a cold saturated alcoholic solution of binitrobenzene, and strong hydrochloric acid added drop by drop, whereupon the liquid in contact with the zinc immediately acquires a fine crimson colour. The action must be continued till the coloured liquid no longer forms a cloud when mixed with water, the zinc being withdrawn whenever the liquid becomes too hot or the action too violent. When the action is complete, the zinc is completely withdrawn; the liquid neutralised with an alkali, the precipitate of oxide of zinc washed on a filter with strong alcohol; the alcoholic filtrate with the washing evaporated over the water-bath; and the residue further purified by washing with water, then redissolved in alcohol and again evaporated.

*Properties.* Black shining, brittle crust, easily removed from the containing vessel. Its alcoholic solution is perfectly transparent to transmitted light, but by reflected light it appears absolutely opaque and of a fine orange-red colour, as if it held vermilion in suspension. — This phenomenon is well seen by the flame of alcohol saturated with a baryta-salt, or better by the solar spectrum, the red ray producing no effect.

| | | | Church & Perkin. |
|---|---|---|---|
| 12 C | 72 | 59·01 | 59·04 |
| 2 N | 28 | 22·95 | 22·80 |
| 6 H | 6 | 4·92 | 4·68 |
| 2 O | 16 | 13·12 | 13·48 |
| $C^{12}N^2H^6O^2$ | 122 | 100·00 | 100·00 |

Nitrosaniline cannot be volatilised without decomposition: at a higher temperature, it becomes carbonised and gives off a white vapour. Heated

with soda-lime, it gives off all its nitrogen in the form of ammonia and aniline. It is decolorised by the prolonged action of nascent hydrogen. Nitrosaniline is nearly insoluble in water, but dissolves readily in acids. With dilute sulphuric and nitric acids, it forms solutions of a deep crimson colour; boiling nitric acid dissolves it with yellow colour; and fuming sulphuric acid, with an intense brown colour, which nearly disappears on addition of water. It likewise dissolves, with splendid crimson colour, in highly concentrated hydrochloric acid, and the solution gradually deposits the colouring matter in the form of a reddish film having the brilliant metallic lustre of copper. The same solution exposed to the air forms after a while a gummy mass, while a portion of the nitrosaniline separates. Alkalis precipitate nitrosaniline from its acid solutions in brownish-yellow flakes, but if the action of the alkali be not long continued, the original crimson colour reappears on the addition of an acid.

Nitrosaniline dissolves readily in *alcohol*. ¶.

*Azonitro-nucleus* $C^{12}NXH^4$.

## Nitraniline.

$$C^{12}N^2H^6O^4 = C^{12}NXH^4H^2.$$

HOFMANN & MUSPRATT. (1846.) *Ann. Pharm.* 57, 201; also *Phil. Mag. J.* 29, 312.
E. ARPPE. *Ann. Pharm.* 90, 147; 93, 157.

*Preparation.* 1. *Modification a.* — The *Paranitraniline* of Arppe. — The aqueous solution of binitrobenzene (p. 204) is saturated with ammoniacal gas; sulphuretted hydrogen passed through the blood-red liquid, till the liquid is saturated with it and only a slight deposition of sulphur takes place; and the solution then mixed with hydrochloric acid and evaporated, whereupon an additional quantity of sulphur separates, together with undecomposed binitrobenzene. The filtrate is then mixed with potash, which precipitates a brown adhesive resin; this resin freed from potash, by washing with cold water, and then dissolved in boiling water; the orange-yellow solution filtered to separate a small quantity of undissolved brown resin; and the needles of nitraniline which separate on cooling, purified by recrystallisation from hot water. (Hofmann & Muspratt.) Arppe further purifies the crystals with animal charcoal.

*Modification β.* — *Nitraniline* of Arppe. — Pyrotartonitranil ($C^{22}N^2H^{10}O^8$) is dissolved in a boiling dilute solution of carbonate of soda, mixed with a little caustic soda, whereby it is converted, by taking up 2 At. water, into pyrotartonitranilic acid, and the solution boiled till it no longer gives a precipitate of pyrotartonitranilic acid on addition of nitric acid. The pyrotartonitranilic acid is then resolved into nitraniline β, and pyrotartaric acid:

$$C^{22}N^2H^{12}O^{10} = C^{12}N^2H^6O^4 + C^{10}H^6O^6.$$

The yellow solution yields on cooling an abundant crop of yellow rhombic tables, which must be collected on a filter, washed with cold water, and purified by recrystallisation. (Arppe.)

*Properties.* *a.* Needles of a fine yellow colour and an inch long; heavier than water. They melt at about 110° (at 108°, according to Arppe), forming an oil of a deep yellow colour, which boils at 285°, passes over in yellow vapours, and solidifies in the receiver, forming a laminated mass; at 100°, the crystals sublime in beautiful laminæ, without previous fusion. (Hofmann & Muspratt.) — ¶. The sublimed crystals are rhombic tables of 51° and 129°, having one of the acute angles either perpendicularly truncated or bevelled with two faces, while the two obtuse angles are sometimes obliquely truncated, sometimes unaltered; macles are often formed with deep re-entering angles. Similar modifications are exhibited by the crystals obtained from solution in water or alcohol. (Arppe.) ¶. — The crystals are inodorous at ordinary temperatures, but when slightly warmed, they emit an aromatic odour having a distant resemblance to that of aniline; they have a burning sweet taste. They are perfectly neutral, and colour firwood (as well as the cuticle) deep yellow, like aniline, but do not produce any blue colour with chloride of lime. (Hofmann & Muspratt.)

¶. *β.* Crystallises from the aqueous solution by slow cooling in long needles; but by more rapid cooling, in small tabular or needle-shaped crystals with angles of 69° and 111°, having the smaller angle truncated in such a manner as to produce a six-sided table with angles of 111° and 138°. From an alcoholic solution, the rhombic tables separate unaltered together with the six-sided tables; an ethereal solution yields sometimes tables, sometimes capillary needles; from an aqueous solution containing carbonate of soda, rhombic tables of 55° and 125° are obtained; by sublimation, sometimes needles, sometimes irregular laminæ. The crystals melt at 141°, volatilise at about the same temperature, and sublime very beautifully when heated between two watch-glasses. At 100°, the sublimation is scarcely perceptible. The crystals *β* have also scarcely any taste. (Arppe.)

| | | | Hofmann & Muspratt. | Arppe. | |
|---|---|---|---|---|---|
| | | | *α.* | *α.* | *β.* |
| 12 C | 72 | 52·17 | 52·25 | 52·01 | 52·03 |
| 2 N | 28 | 20·29 | 20·52 | | |
| 6 H | 6 | 4·35 | 4·54 | 4·37 | 4·40 |
| 4 O | 32 | 23·19 | 22·69 | | |
| $C^{12}N^2H^6O^4$ | 138 | 100·00 | 100·00 | | |

*Decompositions.* 1. The vapour of nitraniline burns with a bright sooty flame. — 2. Nitraniline *α* distils when heated almost without residue; *β* leaves a very considerable quantity of carbonaceous matter. (Arppe.) — 3. Bromine converts nitraniline with great rise of temperature and evolution of hydrobromic acid gas, into a brown resin whose solution in hot alcohol deposits yellowish neutral crystals, insoluble in water, acids, and alkalis, and probably consisting of nitrobromaniline $C^{12}NXBr^2H^4$. (Hofman & Muspratt.) — 4. *Nitric acid* acts violently on nitraniline *α*, and converts it after long boiling into an acid which appears to be picric acid. (Hofmann & Muspratt.) — Nitraniline *β* is dissolved by nitric acid, even in the highly concentrated state, without visible decomposition. (Arppe.) — 5. *Gaseous chloride* of *cyanogen* passed through

melted nitraniline converts part of it into binitromelaniline, while the greater portion is converted into a resinous substance. Alcoholic nitraniline is decomposed very slowly by chloride of cyanogen, and aqueous nitraniline in a peculiar manner; but nitraniline dissolved in ether forms, with chloride of cyanogen, nothing but hydrochlorate of nitraniline, and yellowish needles of nitraniline-urea. (Hofmann and Muspratt.)

$$2C^{12}N^2H^6O^4 + 2HO + C^2NCl = C^{12}N^2H^6O^4,HCl + C^{14}N^3H^7O^6.$$

6. The solution of nitraniline in bromide of ethyl quickly deposits, even at ordinary temperatures, large pale yellow crystals of hydrobromate of ethylonitraniline ($C^{16}NXH^{10},HBr$).

*Combinations.* Nitraniline dissolves very sparingly in cold, but somewhat copiously in hot *water*. (Hofmann & Muspratt.) Nitraniline $a$ dissolves in 600 pts. of water at 18·5°, much more readily in boiling water; $\beta$ dissolves in 1250 pts. of water at 12·5 and in 45 pts. of boiling water. (Arppe.)

Nitraniline is a very weak base; it does not precipitate any metallic salt, and from its *salts*, some of which are crystallisable, it is precipitated in the crystalline form by aniline as well as by the caustic alkalis and alkaline carbonates.

*Sulphate of a-Nitraniline* forms shining microscopic rhombic tables which have but little taste, and form a perfectly colourless solution in water, from which the base is precipitated in the crystalline state by potash and ammonia.

*Sulphate of β-Nitraniline.* — A solution of $\beta$-nitraniline in dilute sulphuric acid deposits, after gentle evaporation, large shining laminæ of the sulphate; smaller crystals exhibit under the microscope the form of square tables. The salt has a strong sour taste, is decomposed by water, but is not altered by exposure to the air. The *bi-acid salt* $C^{12}NH^6O^4 + 2(HO,SO^3)$ contains 34·41 p. c. sulphuric acid. (Arppe.)

*Hydrochlorate of a-Nitraniline.* — The colourless solution of the base in hydrochloric acid, yields by evaporation, nacreous crystals, extremely soluble in water and alcohol. (Hofmann & Muspratt.) Elongated rhombic tables with angles of 120° and 60°, which are permanent in the air and dissolve readily in hydrochloric acid; they are decomposed by water, which separates the greater part of the base. (Arppe.)

*Hydrochlorate of β-Nitraniline.* — $\beta$-nitraniline forms with boiling hydrochloric acid, a yellow solution, or if the acid is in great excess, a colourless solution, which, on cooling deposits rather large, colourless, tabular crystals, which in their simplest form, are four-sided tables, with angles either ($a$) of 95° and 85°, or ($b$) of 65° and 115°; by the combination of these two forms, the acute angles of $a$ being truncated by $b$, six-sided tables are formed; and by the truncation of all the angles of $a$, eight-sided tables. The salt is easily decomposed, both by heat, which causes it to turn yellow and give off acid, and also by water which separates the base almost completely; alkalis precipitate the nitraniline in the crystalline form, but the precipitate redissolves in excess of the alkali. (Arppe.)

| | | | Hofmann & Muspratt (a). | Arppe (β). |
|---|---|---|---|---|
| 12 C | 72·0 | 41·28 | | |
| 2 N | 28·0 | 16·06 | | |
| 7 H | 7·0 | 4·01 | | |
| 4 O | 32·0 | 18·35 | | |
| Cl | 35·4 | 20·30 | 20·37 | 20·20 |
| $C^{12}N^2H^6O^4$,HCl | 174·4 | 100·00 | | |

*Nitrate of α-Nitraniline.* — Crystalline powder, easily soluble in water, but sparingly in nitric acid: hence when nitric acid is poured upon the base, a white crystalline powder is produced which disappears on addition of water. (Arppe.) This result is not in accordance with Hofmann & Muspratt's statement that α-nitraniline is violently decomposed by nitric acid.

*Nitrate of β-Nitraniline.* — The base dissolves very readily in warm nitric acid. The salt crystallises in shining needles several lines long and perpendicularly truncated, and is decomposed by water. (Arppe.)

*Chloroplatinate of α-Nitraniline.*—The alcoholic (but not the aqueous) solution of hydrochlorate of α-nitraniline forms with bichloride of platinum, a yellow crystalline precipitate, which must be washed with ether, dissolves readily in water and alcohol, and contains 28·62 p. c. platinum; therefore = $C^{12}NXH^6$,HCl,$PtCl^2$. (Hofmann & Muspratt.)

*Chloroplatinate of β-Nitraniline.* — *a.* $C^{12}NXH^6$,HCl,$PtCl^2$.—A concentrated aqueous or alcoholic solution of bichloride of platinum, is mixed with a warm concentrated solution of hydrochlorate of β-nitraniline; the resulting yellow precipitate collected in an empty glass funnel; the mother-liquor left to drain; and the precipitate washed, first with an alcoholic solution of β-nitraniline, and finally with ether. — Or, the two salts are mixed in the state of concentrated alcoholic solution; the precipitate rinsed with a small quantity of water; and the mother-liquor removed as completely as possible by pressure. — The salt, when dry has a yellow colour. From a concentrated alcoholic solution, it crystallises almost instantly in capillary needles united in stellate groups. May be heated to 100° without decomposition, but at a higher temperature, it takes fire and burns with slight detonation. Dissolves in water, and much more readily in alcohol; soluble also in ether: water added to the alcoholic solution throws down a copious precipitate of the unaltered salt. The aqueous solution is decomposed by evaporation; the alcoholic solution is more stable. The solubility of the salt in water, alcohol, and ether, is increased by the presence of hydrochloric acid. The crystals gave by analysis 28·22 p. c. platinum; the precipitate formed by water in the alcoholic solution, gave 28·45 p. c. (Arppe.)

*b.* $C^{12}NXH^6$,HCl,2$PtCl^2$. — Remains as a yellow less soluble compound when the salt *a* is washed with a mixture of alcohol and ether. Contains 38·16 p. c. platinum. It is partially dissolved by alkalis, forming a red solution; but part remains undissolved in the form of a brick-red powder, which dissolves with red colour in water and in alcohol. The aqueous solution once yielded small regular octohedrons of a red colour. (Arppe.)

*Oxalate of α-Nitraniline.*—An alcoholic solution of α-nitraniline forms with alcoholic oxalic acid, yellowish crystals, which, when washed with ether and dried on a tile, contain 41·30 p. c. C and 3·99 H, and are

therefore $C^{12}NXH^6,HO,C^4H^2O^8$. (Hofmann & Muspratt.) — *Oxalate of β-Nitraniline* crystallises in delicate needles and laminæ: it is an acid, sparingly soluble salt, and forms a yellow solution. (Arppe.)

*Tartrate of α-Nitraniline* forms a yellow solution from which the salt crystallises in yellow rectangular tables. Potash decomposes the solution, separating the base in the form of a yellow crystalline precipitate soluble in excess of the alkali. — *Tartrate of β-Nitraniline* crystallises in yellow needles; potash does not precipitate, but dissolves it, forming a red solution. (Arppe.)

A solution of either modification of hydrochlorate of nitraniline, mixed with a recently prepared infusion of *gall-nuts* and afterwards with a small quantity of potash, yields a copious flocculent or almost gummy precipitate, which is decomposed by excess of potash, a portion of the base being separated in the crystalline form. (Arppe.)

Nitraniline dissolves with red-brown colour in *alcohol* and *ether*. (Hofmann & Muspratt). Both modifications dissolve with facility in alcohol and ether. (Arppe.)

### ¶. *Azonitro-nucleus* $C^{12}NX^2H^3$.

## Binitraniline.

$$C^{12}N^3H^5O^8 = C^{12}NX^2H^3,H^2.$$

GOTTLIEB. *Ann. Pharm.* 85, 17.

*Dinitraniline, Dinitrophenylamine.*

*Formation and Preparation.* By the action of alkalis on citraco-binitranil:

$$\underbrace{C^{22}N^3H^7O^{12}}_{\text{citracobinitranil.}} + 4HO = \underbrace{C^{12}N^3H^5O^8}_{\text{binitraniline.}} + \underbrace{C^{10}H^6O^8}_{\text{citraconic acid.}}$$

When citracobinitranil is treated with a boiling dilute solution of carbonate of soda, carbonic acid is evolved, and the light flocculent crystals of the anil are partly dissolved, and partly converted into a heavy, yellow, crystalline powder consisting of binitraniline; when the action is complete, this substance separates out in more definite crystals. If the boiling be not continued long enough to ensure the complete decomposition of the anil in the manner above-mentioned, the mother-liquor is found to contain citraco-binitranilate of soda as well as citraconate. The binitraniline is purified by crystallising it several times from boiling water.

*Properties.* Crystallises by spontaneous evaporation of its solution in a mixture of alcohol and ether, in greenish-yellow, rather brilliant tables, exhibiting a bluish tint by reflected light on the lateral faces. Inodorous. Boils at 185°, giving off yellow vapours, which condense in the form of a yellow sublimate; the melted portion solidifies on cooling into a deep yellow crystalline mass.

| | *Crystals.* | | Gottlieb. |
|---|---|---|---|
| 12 C | 72 | 39·34 | 39·28 |
| 3 N | 42 | 22·95 | 23·28 |
| 5 H | 5 | 2·74 | 2·80 |
| 8 O | 64 | 34·97 | 34·64 |
| $C^{12}N^3H^5O^8$ | 183 | 100·00 | 100·00 |

Heated suddenly in a tube, it blackens and explodes with facility. — Sulphide of ammonium converts it into amidonitraniline.

$$C^{12}N^3H^5O^8 + 6HS = C^{12}N^3H^7O^4 + 4HO + 6S.$$

Binitraniline dissolves sparingly in cold *water,* but readily in boiling water and in hot *alcohol.*

It does not combine with acids. (Gottlieb.) ¶.

*Azotamidogen-nucleus* $C^{12}NAdH^4$.

## Semibenzidam.

$C^{12}N^2H^8 ? = C^{12}NAdH^4,H^2. ?$

ZININ. (1844.) *J. pr. Chem.* 33, 34.

*Azophenylamine* (Gerhardt), *Azaniline.*

When an alcoholic solution of binitrobenzene (p. 205), is distilled with hydrosulphate of ammonia, there remains, together with a large quantity of precipitated sulphur, a yellowish-brown resinous substance, which is insoluble in water, and separates from boiling alcohol or ether, when left to cool without contact of air, in yellowish flakes.

These flakes contain 8 At. H to 12 At. C; they melt under boiling water into a brown viscid liquid; when exposed to the air, especially in the moist state, they quickly assume a greenish colour; and the yellow solution in alcohol or ether quickly becomes darker on exposure to the air, and deposits a greenish powder.

The compounds of this substance with sulphuric and hydrochloric acid are yellow, easily decomposible salts, nearly insoluble in water, alcohol and ether. (Zinin.)

¶. *Azonitroamidogen-nucleus* $C^{12}NXAdH^3$.

## Amidonitraniline.

$C^{12}N^3H^7O^4 = C^{12}NXAdH^3,H^2.$

GOTTLIEB. *Ann. Pharm.* 85, 27.

*Azophenylamine* (Gottlieb), *Nitrazophenylamine* (Gerhardt).

*Preparation* By the action of sulphide of ammonium on binitraniline (p. 293). When this substance is boiled for about two hours with a large excess of solution of sulphide of ammonium, the liquid acquires a dark red colour, the crystals of binitraniline disappear, and are succeeded by a network of delicate shining dark red needles of amidonitraniline, which gradually increase in quantity and are likewise abundantly deposited after the action is completed and the liquid has cooled. The compound is obtained in the purest state by precipitating it from the hydrochlorate or oxalate purified by several crystallisations, and then recrystallising it two or three times from hot alcohol.

*Properties.* Crystallises in long slender needles united in groups, having a slight red colour when dry, and exhibiting a golden iridescence on their broader faces. When separated by ammonia from a saturated solution of one of its salts, it takes the form of a dull brick-red powder; but dilute solutions deposit it in small, reddish yellow, shining plates. Melts at a high temperature and volatilises in great part without decomposition, forming a woolly sublimate. When suddenly heated, it explodes slightly, leaving a residue of charcoal.

| | | | Gottlieb. |
|---|---|---|---|
| 12 C | 72 | 47·06 | 46·86 |
| 3 N | 42 | 27·45 | 27·69 |
| 7 H | 7 | 4·57 | 4·55 |
| 4 O | 32 | 20·92 | 20·90 |
| $C^{12}N^3H^7O^4$ | 153 | 100·00 | 100·00 |

*Combinations.* Amidonitraniline dissolves readily in *water*, forming a deep red solution.

It combines with *acids*, forming salts which are decomposed by water and by alcohol, with separation of the base: hence in preparing them, it is necessary to let them crystallise in presence of an excess of acid.

*Sulphate of Amidonitraniline*, $C^{12}N^3H^7O^4,HO,SO^3$ is obtained by dissolving the base in warm dilute sulphuric acid, and separates on cooling in yellowish scales, having a fatty lustre and containing 8·20 p. c. sulphur.

A mixture of the solution of this salt with sulphate of alumina, does not yield any double salt when left to evaporate.

*Hydrochlorate of Amidonitraniline.* — May be prepared by boiling the crude base with dilute hydrochloric acid, which dissolves it, leaving only a residue of sulphur and a secondary product of a dull green crystalline aspect, part of which also passes into the solution. To free the salt completely from this impurity, it must be repeatedly dissolved in boiling dilute hydrochloric acid and recrystallised. — From a concentrated acid solution, it separates in yellowish-brown needles; from a dilute solution by spontaneous evaporation, in oblique prisms often 4 or 5 millimetres in length and united in groups. These crystals exhibit a light brownish-green colour by transmitted light, and a peculiar blue iridescence on some of their faces by repeated light. The acid solution has a greenish-brown colour. The crystals contain 2 At. water which they give off at 100°, or in vacuo or over oil of vitriol at ordinary temperatures. At 100°, however partial decomposition takes place and hydrochloric acid is given off.

| *Dried over oil of vitriol.* | | | Gottlieb. |
|---|---|---|---|
| 12 C | 72·0 | 38·00 | 37·78 |
| 3 N | 42·0 | 22·16 | |
| 8 H | 8·0 | 4·22 | 4·24 |
| Cl | 35·4 | 18·73 | 19·17 |
| 4 O | 32·0 | 16·89 | |
| $C^{12}N^3H^7O^4,HCl$ | 189·4 | 100·00 | |

The crystals contain 17·08 p. c. chlorine, and are therefore $C^{12}N^3H^7O^4,HCl + 2\ Aq$.

*Nitrate of Amidonitraniline.* — Warm dilute nitric acid readily dissolves amidonitraniline, but the solution soon acquires a dark colour and deposits flakes indicating partial decomposition. The pure salt may however be obtained by moistening the base with water, and pouring dilute nitric acid upon it by small portions: it it then immediately converted into a thick magma of micaceous scales, which may be freed from the mother-liquor by pressure between paper. The salt thus prepared is anhydrous, and may be kept for months over oil of vitriol without losing its lustre.

| | | | Gottlieb. |
|---|---|---|---|
| 12 C | 72 | 33·33 | 33·78 |
| 4 N | 56 | 25·93 | 26·07 |
| 8 H | 8 | 3·70 | 3·87 |
| 10 O | 80 | 37·04 | 36·28 |
| $C^{12}N^3H^7O^4,HO,NO^5$ | 216 | 100·00 | 100·00 |

A solution of hydrochlorate of amidonitraniline mixed with bichloride of *platinum*, does not yield a double salt, the platinum being rapidly reduced to the metallic state.

*Platinhydrocyanate of Amidonitraniline*, $2(C^{12}N^3H^7O^4,HCy,PtCy) + 5\ Aq$. — Obtained by adding crystallised hydrochlorate of amidonitraniline to a boiling aqueous solution of platinocyanide of magnesium. (viii, 53). The solution separated by filtration from a small quantity of dark insoluble matter, gradually deposits a mixture of the platinhydrocyanate and the free base, which latter may be removed by digestion with a small quantity of dilute hydrochloric acid. — Large laminæ, having a light brownish-yellow colour and strong lustre, and giving off their water at 112°. They cannot be recrystallised from water without partial decomposition.

| *At* 112°. | | | Gottlieb. |
|---|---|---|---|
| 16 C | 96 | 31·48 | 31·74 |
| 5 N | 70 | 22·95 | 23·12 |
| 8 H | 8 | 2·62 | 2·76 |
| Pt | 99 | 32·46 | 32·28 |
| 4 O | 32 | 10·49 | 10·10 |
| $C^{12}N^3H^7O^4,HCy,PtCy$ | 305 | 100·00 | 100·00 |

The compound dried over oil of vitriol leaves when ignited 30·15 p. c. platinum, whence it is $2(C^{12}N^3H^7O^4,HCy,PtCy) + 5Aq$.

*Oxalate of Amidonitranilne.* — Obtained by dissolving the base in aqueous oxalic acid. From concentrated solutions it separates in yellow needles; from more dilute solutions, in brownish-yellow prisms, exhibiting a bluish iridescence on certain faces. It is anhydrous, and dissolves but sparingly in cold water.

| | | | Gottlieb. |
|---|---|---|---|
| 28 C | 168 | 42·43 | 42·83 |
| 6 N | 84 | 21·21 | 21·41 |
| 16 H | 16 | 4·04 | 4·20 |
| 16 O | 128 | 32·32 | 31·56 |
| $2C^{12}N^3H^7O^4,C^4H^2O^8$ | 396 | 100·00 | 100·00 |

Amidonitraniline dissolves in *alcohol* and *ether*, forming deep red solutions. (Gottlieb.) ¶.

*Conjugated Compounds of* 1 *At.* $C^{12}NH^5$ *or a similar Nucleus.*

## Sulphanilic Acid.

$C^{12}NH^7S^2O^6 = C^{12}NH^7,2SO^3$.

GERHARDT. *N. J. Pharm.* 10, 5; abstr. *Compt. rend.* 21, 285.

*Anilinschwefelsäure, Sulfanilinsäure, Acide sulfanilique, Phenylsulphamic acid.*

*Formation.* By heating oil of vitriol with aniline, formanilide, oxanilide (Gerhardt), carbanilide or aniline-urea (Hofmann), or by boiling sulphobenzolic acid with nitric acid, and treating the resulting nitrosulphobenzolic acid, $C^{12}XH^5,2SO^3$ with sulphuretted hydrogen, after combining it with ammonia; it is thereby converted into sulphanilate of ammonia. (Laurent, *Compt. rend.* 31, 538.)

*Preparation.* 1. A solution of aniline in a slight excess of sulphuric acid is evaporated to dryness; the residue heated, cautiously and with constant stirring, as long as water and aniline continue to escape, and crystallised from boiling water. — 2. Better: the mixture of formanilide and oxanilide which remains after heating oxalate of aniline to 180°, is mixed with oil of vitriol to the consistence of a thick pulp; this mixture heated in a flask, but so gently that no blackening shall take place, and as long as carbonic acid and carbonic oxide continue to escape with effervescence; the residue exposed in a shallow dish to a moist atmosphere; the crystalline mass suspended in and washed with cold water, and recrystallised from boiling water. (Gerhardt.) — 3. The solution of aniline-urea in oil of vitriol is gently heated; the brownish mixture of sulphate of ammonia and sulphanilic acid, which forms, with evolution of carbonic acid, washed with water; and the crystalline mass thus produced, washed with animal charcoal and crystallised from hot water. (Hofmann, *Ann. Pharm.* 70, 133.)

*Properties.* Colourless, rhombic tables, having a strong lustre and a very sour taste.

| *Crystals.* | | | Gerhardt. | Hofmann. |
|---|---|---|---|---|
| 12 C | 72 | 41·62 | 41·95 | |
| N | 14 | 8·09 | 8·60 | |
| 7 H | 7 | 4·05 | 4·33 | |
| 2 S | 32 | 18·49 | 18·90 | 18·75 |
| 6 O | 48 | 27·75 | | |
| $C^{12}NH^7,2SO^3$ | 173 | 100·00 | | |

*Decompositions.* 1. The acid, when subjected to dry distillation, becomes carbonised, melts, and gives off a large quantity of sulphurous acid, together with an oil which solidifies on cooling, and forms with water, sulphite of aniline. — 2. The aqueous solution of sulphanilic acid mixed with *chlorine*-water, assumes a pale carmine-colour, gradually changing to brown-red. — 3. The same solution, even when very dilute, becomes milky on addition of *bromine*-water, and yields after a while, a white curdy precipitate insoluble in potash.— 4. The solution is coloured brown-red by *chromic acid*.— 5. Cold concentrated nitric acid does not act upon sulphanilic acid; but hot nitric acid, forms, with great evolution of gas, a red solution which deposits a resin when left at rest.— 6. Anhydrous *sulphuric acid* carbonises the greater part of sulphanilic acid, in spite of external cooling. —7. When the acid is heated with *potash-lime,* pure aniline distils over, and a sulphate is left behind. In the case of other anilides also, the nitrogen cannot be determined (according to Will & Varrentrapp's method) by means of potash-lime. (Gerhardt.)

*Combinations.* The acid dissolves sparingly in cold, more abundantly in boiling *water*. (Gerhardt.)

*Sulphanilates.* The acid decomposes alkaline carbonates with effervescence; it neutralises bases perfectly, and is separated by mineral acids from the concentrated solutions of its salts, in slender needles. (Gerhardt.)

*Sulphanilate of Ammonia.* — The solution of the acid in aqueous ammonia yields by spontaneous evaporation, highly lustrous, thin, six-sided or rectangular tables, which become dull at 100°, and at a higher temperature, yield sulphurous acid and the same oil as the free acid. (Gerhardt.)

| *Crystals at* 100°. | | | Gerhardt. |
|---|---|---|---|
| 12 C | 72 | 37·89 | 37·6 |
| 2 N | 28 | 14·74 | |
| 10 H | 10 | 5·26 | 5·4 |
| 2 $SO^3$ | 80 | 42·11 | |
| $C^{12}NH^6(NH^4),2SO^3$ | 190 | 100·00 | |

*Sulphanilate of Soda.* — The aqueous acid neutralised with carbonate of soda, crystallises by spontaneous evaporation in large eight-sided tables, whereas from boiling alcohol (which leaves a small quantity of carbonate of soda mixed with the salt) needles are obtained. The tabular crystals contain 14·65 p. c. (4 At.) water; when heated, they give

off the water with fusion and intumescence; then turn brown; evolve stinking vapours together with a brown oil containing aniline; and, when heated in the air, yield a blue flame and sulphurous acid. On one occasion, large prisms were obtained, containing 53·6 p.c. (24 At.) water of crystallisation. (Gerhardt.)

| *Dried at* 100°. | | | Gerhardt. |
|---|---|---|---|
| 12 C | 72·0 | 36·88 | 36·9 |
| N | 14·0 | 7·17 | |
| 6 H | 6·0 | 3·08 | 3·2 |
| Na | 23·2 | 11·89 | 11·4 |
| 2 S | 32·0 | 16·39 | 17·0 |
| 6 O | 48·0 | 24·59 | |
| $C^{12}NH^6(NH^4),2SO^3$ | 195·2 | 100·00 | |

*Sulphanilate of Baryta.* $C^{12}NH^6Ba,2SO^3$.—Rectangular prisms, somewhat freely soluble in water (Gerhardt), containing 28·40 p.c. barium. (Buckton & Hofmann.)

*Sulphanilate of Copper.* — Protoxide of copper dissolves very slowly, but the hydrate, readily, in the aqueous acid, forming a green liquid, which, by evaporation and cooling, yields short, hard, blackish-green prisms having a strong lustre. These crystals, when heated above 100°, give off their water and assume a dingy yellow colour, and at a higher temperature swell up in vermiform masses.

| *Crystals.* | | | Gerhardt. |
|---|---|---|---|
| 12 C | 72 | 30·00 | 30·5 |
| N | 14 | 5·84 | |
| 10 H | 10 | 4·17 | 4·2 |
| Cu | 32 | 13·33 | 13·0 |
| 2 S | 32 | 13·33 | |
| 10 O | 80 | 33·33 | |
| $C^{12}N^6Cu,2SO^3 + 4Aq$ | 240 | 100·00 | |

*Sulphanilate of Silver.* $C^{12}N^6Ag,2SO^3$.— Shining scales (Gerhardt), containing, when dried at 120°, 38·58 p.c. silver. (Buckton & Hofmann.)

*Sulphanilate of Aniline.* — Aqueous aniline, saturated while hot with sulphanilic acid, yields on cooling, needles consisting of the free acid, and afterwards on evaporating the mother-liquor, laminæ of the aniline-salt.

Sulphanilic acid dissolves in *alcohol* less easily than in water. (Gerhardt.)

## ¶. Bisulphanilic Acid.

$C^{12}NH^7S^4O^{12} = C^{12}NH^7,4SO^3$.

G. B. Buckton & A. W. Hofmann. *Chem. Soc. Qu. J.* 9, 259.

***Disulphanilic acid, Phenyldisulphamic acid.***

Obtained by the action of fuming sulphuric acid on sulphanilic acid. Dry and finely pulverised sulphanilic acid is stirred up with fuming sulphuric acid to the consistence of a thin paste; the mixture heated in an air-bath to between 160° and 170°, at which temperature sulphurous acid just begins to escape; and the digestion continued for about seven hours, or till a portion taken out on a glass rod no longer solidifies on cooling. The mass, which has the consistence of treacle, is then dissolved in cold water, and separated by filtration from a black insoluble, apparently crystalline substance.

Bisulphanilic acid separated from the lead-salt by sulphuretted hydrogen has a very acid and pungent taste; it crystallises with great difficulty, but is precipitated in white grains from a strong aqueous solution by addition of alcohol; the precipitation is facilitated by adding a little ether.

| | *Calculation.* | |
|---|---|---|
| 12 C | 72 | 28·46 |
| N | 14 | 5·53 |
| 7 H | 7 | 2·76 |
| 4 S | 64 | 25·30 |
| 12 O | 96 | 37·95 |
| $C^{12}NH^7,4SO^3$ | 253 | 100·00 |

May also be regarded as $C^{12}H^5Ad,4SO^3$.

Bisulphanilic acid is easily soluble in *water*.

The *Bisulphanilates* contain $C^{12}NH^5M^2,4SO^3$. The barium and silver-salts are soluble in water, but insoluble in alcohol and ether.

*Bisulphanilate of Baryta.* — The aqueous acid obtained as above, is saturated with carbonate of baryta, the liquid evaporated to dryness, whereby a further separation of the black substance is effected, the baryta-salt redissolved, the solution treated with a small quantity of alcohol, which precipitates a small quantity of sulphanilate of baryta, and the filtrate evaporated either over the water-bath, whereby a horny fissured mass, is left, or in vacuo, whereby the salt is obtained in microscopic crystals.

| | | | Buckton & Hofmann. |
|---|---|---|---|
| 12 C | 72·0 | 18·58 | |
| N | 14·0 | 3·60 | |
| 5 H | 5·0 | 1·28 | |
| 2 Ba | 137·2 | 35·30 | 35·30 |
| 4 S | 64·0 | 16·49 | 16·32 |
| 12 O | 96·0 | 24·75 | |
| $C^{12}NH^5Ba^2,4SO^3$ | 388·2 | 100·00 | |

The salt heated on platinum foil, blackens without inflaming. Heated in close vessels, it yields a vapour which sublimes in beautiful crystals, probably of sulphite of aniline. It is decomposed by strong nitric acid, yielding sulphate of baryta, and a yellow liquid, which when evaporated, leaves crystals having a very bitter taste.

*Bisulphanilate of Silver.* $C^{12}NH^5Ag^2,4SO^3$. — By saturating the aqueous acid with carbonate of silver, and precipitating with a mixture

of alcohol and ether, the salt is precipitated in colourless crystalline granules; the precipitation is accelerated by stirring. By spontaneous evaporation, the salt is obtained in small tabular crystals which blacken when boiled with water. They contain 45·53 per cent. of silver. (Buckton & Hofmann.)

Bisulphanilic acid is insoluble it alcohol and ether. ¶.

## Methaniline.

$$C^{14}NH^9 = C^{12}(C^2H^3)NH^4,H^2.$$

A. W. Hofmann. (1850.) *Ann. Pharm.* 74, 150.

*Methylaniline, Methylophenylamine, Formaniline.*

*Preparation.* The mixture of aniline or excess of iodide (or bromide) of methyl, which must be made gradually to prevent too great a rise of temperature, yields crystals of hydriodate (or hydrobromate) of methaniline, from the aqueous solution of which salts, the oily base may be separated by potash.

*Properties.* Transparent oil, which boils at 192°, has a peculiar odour, and colours aqueous chloride of lime violet, but not so strongly as aniline.

The salts of methaniline are sparingly soluble in water, and are separated from their aqueous solution in the crystalline state by acids.

The *chloroplatinate* is precipitated in the form of a limpid oil, quickly changing to pale yellow crystalline scales which must be quickly washed with cold water and dried. They soon turn black from decomposition, and when alcoholic solutions are used, a black mass is immediately precipitated. The crystals contain 31·55 p. c. platinum, and are therefore $C^{14}NH^9,HCl,PtCl^2$.

The oxalate crystallises readily, but quickly decomposes, reproducing aniline. (Hofmann.)

## Formanilide.

$$C^{14}NH^7O^2 = C^{12}(C^2H)AdH^4,O^2. ?$$

Gerhardt. (1845.) *N. Ann. Chim. Phys.* 14, 120 and 15, 88; also *N. J. Pharm.* 8, 58; also *J. pr. Chem.* 35, 295. — *N. J. Pharm.* 9, 409.

*Formation* (p. 262).

*Preparation.* The mixture of formanilide and oxanilide obtained by heating oxalate of aniline to between 160° and 180°, is treated with cold alcohol to extract the former; the solution partially evaporated and

separated from a brown product formed from the oxalate of aniline by the action of the air; and the formanilide obtained by further evaporation, first in colourless oily drops which sink to the bottom, and afterwards by evaporation in prisms.

*Properties.* Flat, acuminated, rectangular prisms resembling urea; melts at 46°, into an oil which gives off vapours even at 100°, remains liquid much below 46°, but if then stirred with a glass rod, instantly solidifies. Slightly bitter, neutral.

| | *After fusion at* 100°. | | Gerhardt. |
|---|---|---|---|
| 14 C | 84 | 69·42 | 69·15 |
| N | 14 | 11·57 | |
| 7 H | 7 | 5·79 | 6·10 |
| 2 O | 16 | 13·22 | |
| $C^{14}NH^7O^2$ | 121 | 100·00 | |

Metameric with benzamide.

*Decompositions.* 1. With hot oil of vitriol, formanilide forms sulphanilic acid, without blackening, but with evolution of carbonic oxide.

$$C^{14}NH^7O^2 + 2SO^3 = 2CO + C^{12}NH^7,2SO^3.$$

Dilute sulphuric acid heated with formanilide eliminates formic acid. — 3. Dilute chromic acid mixed with formanilide turns green after a while, but when the mixture is boiled, with addition of sulphuric acid, a precipitate is quickly formed of the same nature as with aniline. — 4. Cold potash-ley does not act upon it, but boiling potash eliminates aniline in a few seconds.

*Combinations.* Aniline dissolves with tolerable facility in water, especially in hot water. It melts under water even below 46°, and remains liquid for several days after cooling. (Gerhardt.)

## Anilocyanic Acid.

$$C^{14}NH^5O^2 = C^{12}CyH,O^2.$$

A. W. HOFMANN. (1850.) *Ann. Pharm.* 74, 9.

*Formation.* By the dry distillation of melanoximide, sparingly by that of oxalate of melaniline. Not by distilling sulphocarbolate of baryta with cyanate of potash, or by distilling anthranilic acid or salicylamide with phosphoric acid.

*Preparation.* Well dried melanoximide is subjected to dry distillation in perfectly dry vessels; and the pale yellow distillate cooled, filtered to separate it from the crystallised carbanilide, and rectified in a tube, moisture being carefully excluded throughout the whole series of operations.

*Properties.* — Thin, transparent, colourless, strongly refracting liquid, heavier than water, boiling at 178° and finally at 180°, having an extremely powerful odour of cyanogen, hydrocyanic acid and aniline together, exciting a copious flow of tears, and producing suffocation in the throat when inhaled.

| | | | | Hofmann. |
|---|---|---|---|---|
| 14 C | 84 | 70·58 | | 70·02 |
| N | 14 | 11·77 | | 11·92 |
| 5 H | 5 | 4·20 | | 4·37 |
| 2 O | 16 | 13·45 | | 13·69 |
| $C^{14}NH^5O^2$ | 119 | 100·00 | | 100·00 |

$= C^{12}NH^2$ (cyanic acid) $+ C^{12}H^4$. (Hofmann.)

*Decompositions.* 1. With *oil of vitriol,* the acid is resolved into carbonic oxide and sulphanilic acid :

$$[C^{14}NH^5O^2 + 2SO^3 = 2CO + C^{12}NH^5,2SO^3.]$$

2. With *hydrochloric acid,* it is resolved into carbonic acid and hydrochlorate of aniline :

$$C^{14}NH^5O^2 + 2HO + HCl = 2CO^2 + C^{12}NH^7,HCl.$$

3. With *water,* into carbonic acid and crystallising carbanilide;

$$2C^{14}NH^5O^2 + 2HO = 2CO^2 + C^{26}N^2H^{12}O^2.$$

4. With *potash-ley,* it is quickly resolved into carbonate of potash and free aniline :

$$C^{14}NH^5O^2 + 2HO + 2KO = 2(KO,CO^2) + C^{12}NH^7.$$

5. With *ammonia,* it evolves great heat, and immediately solidifies in the form of aniline-urea :

$$C^{12}NH^5O^2 + NH^3 = C^{14}N^2H^8O^2.$$

6. With *aniline* it becomes heated, and immediately solidifies in the form of carbanilide :

$$C^{14}NH^5O^2 + C^{12}NH^7 = C^{26}N^2H^{12}O^2.$$

7. Its clear solution in *wood-spirit, alcohol, fusel-oil,* or *carbolic acid,* the formation of which is attended with great evolution of heat, quickly deposits beautiful crystals, which melt at 100°, are insoluble in water, but dissolve readily in alcohol or ether. These crystals appear to be mixtures. Those obtained from wood-spirit contain 63·40 p. c. C and 7·38 H, and are therefore perhaps $C^{16}NH^9O^4$ [ $= C^{12}(C^2H^3)AdH^4,2CO^2$]. Those from alcohol contain 66·74 p. c. C and 6·65H, and are therefore perhaps $C^{18}NH^{11}O^4 =$ [$C^{12}(C^4H^5)AdH^4,2CO^2$]. According to this, the crystals should be analogous to the compound ethers of the amidogen acids (vii, 220.) (Hofmann.)

## ¶. Cyanilide.

$$C^{14}N^2H^6 = C^{12}CyAdH^4.$$

Cahours & Cloez. *Compt. rend.* 38, 355.

When pure and very dry gaseous chloride of cyanogen is passed into a solution of aniline into anhydrous ether cooled with ice, a crystalline deposit is formed, consisting of hydrochlorate of aniline which continually increases; and the filtrate evaporated over the water-bath, leaves cyanilide in the form of a viscid mass which solidifies as it cools.

Reddish substance resembling colophonium in friability, concho̊ïdal fracture and translucence. It is completely decomposed by heat, yielding various products. Its alcoholic solution mixed with hydrochlorate of aniline and evaporated for some time over the water-bath, yields crystallised hydrochlorate of melaniline:

$$C^{12}NH^7 + C^{14}N^2H^6 = \underbrace{C^{26}N^3H^{13}}_{\text{melaniline}}.$$

Cyanilide is insoluble in water, but dissolves readily in alcohol and ether. *Water* added to the alcoholic or ethereal solution, immediately separates a viscous substance which gradually becomes crystalline. (Cahours & Cloez.) ¶.

## Aniline-urea.

$$C^{14}N^2H^8O^2 = C^{12}CyAdH^4,H^2O^2.$$

A. W. Hofmann. (1845.) *Ann. Pharm.* 53, 57; 57, 265; 70, 130; 74, 14.

*Abnormal Cyanate of Aniline, Carbamide-carbanilide, Carbanilamide.*

*Formation.* 1. From vapour of cyanic acid and aniline (p. 253). — 2. From dissolved cyanate of potash and sulphate of aniline (p. 253). — 3. From volatile chloride of cyanogen and aniline in presence of water (p. 253). — 4. From anilocyanic acid and ammonia (p. 302.)

*Preparation.* The vapour of cyanic acid evolved from heated cyanuric acid is passed into anhydrous aniline which must be kept as cool as possible; the resulting crystalline mass dissolved in hot water; and the solution filtered from carbanilide (which is produced more abundantly in proportion as the aniline has been more strongly heated), and cooled to the crystallising point. — 2. Aqueous sulphate or hydrochlorate of aniline is mixed with aqueous cyanate of potash, and the aniline-urea, which is but sparingly soluble in water, separated from the potash-salt in the crystalline mass which forms after a few hours, by recrystallisation. — 3. Aniline is mixed with an aqueous solution of volatile chloride of cyanogen (obtained by passing chlorine gas through aqueous hydrocyanic acid) and the crystallised needles which are contaminated with hydrochlorate

of aniline and a small quantity of melaniline, purified by animal charcoal and two crystallisations from hot water.

*Properties.* Colourless fusible needles and laminæ.

| | | | | | Hofmann. |
|---|---|---|---|---|---|
| 14 C | 84 | .... | 61·76 | ........ | 61·45 |
| 2 N | 28 | .... | 20·58 | ........ | 20·51 |
| 8 H | 8 | .... | 5·89 | ........ | 6·11 |
| 2 O | 16 | .... | 11·77 | ........ | 11·93 |
| $C^{14}N^2H^8O^2$ | 136 | .... | 100·00 | ........ | 100·00 |

$CNH^2O$ (carbamide) + $C^{13}NH^6O$ (carbanilide).

*Decompositions.* — 1. Aniline-urea heated above its melting point, gives up its ammonia with violence, solidifies into a crystalline of carbanilide and cyanuric acid, which latter may be dissolved out by boiling water. This mixture fuses again at a higher temperature and yields a distillate containing carbanilide:

$$6C^{14}N^2H^8O^2 = 3NH^3 + 3\underbrace{C^{26}N^2H^{12}O^2}_{\text{carbanilide.}} + \underbrace{C^6N^3H^3O^6}_{\text{cyanuric acid.}}.$$

2. When gently heated with oil of vitriol, it rapidly evolves carbonic acid and leaves sulphanilic acid and sulphate of ammonia:

$$C^{14}N^2H^8O^2 + 2HO + 4SO^3 = 2CO^2 + C^{12}NH^7,2SO^3 + NH^3,2SO^3.$$

3. When boiled with potash-ley, or more quickly when fused with hydrate of potash, it gives off ammonia and aniline, and leaves carbonate of potash:

$$C^{14}N^2H^8O^2 + 2HO + 2KO = NH^3 + C^{12}NH^7 + 2(KO,CO^2).$$

It is not decomposed by boiling with dilute acids and alkalis.

*Combinations.* Aniline-urea dissolves sparingly in cold, abundantly in boiling *water,* and when immersed in a small quantity of boiling water, melts into a heavy oil.

Dissolves without decomposition in cold *oil of vitriol.*

Dissolves in *nitric acid,* but scarcely more readily than in water, and (unlike urea) crystallises therefrom free from nitric acid.

It does not form any double salt with bichloride of platinum or any crystalline compound with oxalic acid.

It dissolves readily in *alcohol* and *ether.* (Hofmann.)

## Nitraniline-urea.

$$C^{14}N^3H^7O^6 = C^{12}CyAdXH^3,H^2O^2.$$

A. W. Hofmann. *Ann. Pharm.* 67, 156; 70, 137.

Produced, together with binitromelaniline, by the action of volatile chloride of cyanogen on nitraniline dissolved in ether. The resulting needles are purified by crystallisation from hot water.

Long yellow needles.

| | | | | | | Hofmann. |
|---|---|---|---|---|---|---|
| 14 C | ........................ | 84 | .... | 46·41 | ........ | 46·10 |
| 3 N | ........................ | 42 | .... | 23·20 | | |
| 7 H | ........................ | 7 | .... | 3·87 | ........ | 4·16 |
| 6 O | ........................ | 48 | .... | 26·52 | | |
| $C^{14}N^3H^7O^6$ | ................ | 181 | .... | 100·00 | | |

## Ethaniline.

$C^{16}NH^{11} = C^{12}(C^4H^5)NH^4,H^2$.

A. W. Hofmann. (1850.) *Ann. Pharm.* 74, 128; *Chem. Soc. Qu. J.* 3, 285.

*Ethylaniline, Ethylophenylamine, Vinaniline.*

*Preparation.* A mixture of aniline and excess of bromide of ethyl, gently heated in an apparatus which allows the condensed vapours to flow back again, passes into spontaneous ebullition, and afterwards on cooling yields crystals of hydrobromate of ethaniline :

$$C^{12}NH^7 + C^4H^5Br = C^{16}NH^{11},HBr.$$

The mother-liquor retains a portion of the salt dissolved in bromide of ethyl. If the quantity of bromide of ethyl is deficient, the crystals are contaminated with hydrobromate of aniline. The aqueous solution of the hydrobromate of ethaniline is mixed with concentrated potash, and the brown oil which rises to the surface removed with the pipette, dried over hydrate of potash, and rectified.

*Properties.* Transparent, colourless, strongly refracting oil of sp. gr. 0·954 at 18°; boils constantly at 204°; smells like aniline; does not produce any blue colour with chloride of lime; colours firwood and elder-pith yellow, but much less strongly than aniline :

| | | | | | | Hofmann. |
|---|---|---|---|---|---|---|
| 16 C | ........................ | 96 | .... | 79·34 | ........ | 79·28 |
| N | ........................ | 14 | .... | 11·57 | | |
| 11 H | ........................ | 11 | .... | 9·09 | ........ | 9·27 |
| $C^{18}NH^{11}$ | .................... | 121 | .... | 100·00 | | |

$= C^{12}H^5,C^4H^5,H,N.$ (Hofmann.)

*Decompositions.* 1. Ethaniline quickly turns brown when exposed to the air, or even under the mere influence of light. — 2. With *bromine* it forms a neutral (terbromaniline ?) and a basic compound. — 3. It takes fire in contact with dry *chromic acid.* — 4. With phosgene gas it acts violently, forming a hydrochlorate and an indifferent oil. — 5. With *bisulphide of carbon,* it slowly gives off sulphuretted hydrogen. — 6. *Cyanogen-gas* passed through alcoholic ethaniline, forms short prisms probably consisting

of cyanethaniline $C^{18}N^2H^{11}$. This compound is separated in the pulverulent form, on adding ammonia to the solution of the crystals in dilute sulphuric acid: its solution in sulphuric acid, on being mixed with strong hydrochloric acid deposits the hydrochlorate in beautiful crystals; its platinum-salt is very soluble. — 7. Ethaniline absorbs gaseous *chloride of cyanogen* rapidly and with rise of temperature, and then solidifies on cooling in the form of a resinous mixture of a neutral oil and the hydrochlorate of a volatile oily base. — 8. Ethaniline heated for two days in the water-bath with iodide of methyl, yields crystals of hydriodate of metethaniline:

$$C^{16}NH^{11} + C^2H^3I = C^{18}NH^{13},HI.$$

9. Ethaniline mixed with bromide of ethyl, forms in five days, and more quickly if moderately heated, tabular crystals of hydrobromate of biethaniline, the mixture acquiring first a pale yellow, and afterwards a brown colour:

$$C^{16}NH^{11} + C^4H^5Br = C^{20}NH^{15},HBr.$$

10. Similarly, ethaniline heated for two days in the water-bath with bromide of amyl, forms hydrobromate of ethamylaniline.

*Combinations.* The salts of ethaniline dissolve very easily in water, less easily in alcohol from which also they crystallise better. The sulphate and hydrochlorate have not yet been obtained in the solid form.

*Hydrobromate of Ethaniline.* — Preparation (p. 305). Crystallises from the alcoholic solution by spontaneous evaporation in large tables, which at a gentle heat sublime in needles without decomposition, but when quickly heated, are resolved into aniline and bromide of ethyl. They dissolve very readily in water. Contain 40·24 p. c. hydrobromic acid, and are therefore $C^{16}NH^{11},HBr$.

*Chloride of mercury* and *terchloride of gold,* added to hydrochlorate of ethaniline, throw down yellow oils which quickly decompose.

*Chloroplatinate of Ethaniline.* — A saturated aqueous solution of hydrochlorate of ethaniline, added to a concentrated solution of bichloride of platinum, throws down an oil of a deep orange-yellow colour, which, after a few hours, solidifies in the crystalline form; a somewhat more dilute mixture deposits after a few hours, splendid needles an inch long, which must be washed with a mixture of ether and a little alcohol. The crystals are permanent at 100°, and dissolve very readily in water and alcohol.

| | *Crystals at* 100°. | | Hofmann. |
|---|---|---|---|
| 16 C | 96·0 | 29·34 | 29·24 |
| N | 14·0 | 4·28 | |
| 12 H | 12·0 | 3·67 | 3·83 |
| Pt | 99·0 | 30·25 | 30·07 |
| Cl | 106·2 | 32·46 | |
| $C^{16}NH^{11},HCl + PtCl^2$ | 327·2 | 100·00 | |

Ethaniline is soluble in alcohol. (Hofmann.)

## Metethaniline.

$$C^{18}NH^{13} = C^{12}(C^4H^5)(C^2H^3)NH^3,H^2.$$

A. W. Hofmann. (1850.) *Ann. Pharm.* 74, 152; *Chem. Soc. Qu. J.* 3, 296.

*Methylethylaniline, Methylethylophenylamine, Formevinanilin,* — (*Formation,* (p. 306).

Ethaniline mixed with iodide of methyl yields, after being heated for two days in the water-bath, crystals of hydriodate of metethaniline.

The base separated from the crystals smells like ethaniline, but does not produce any colour with chloride of lime.

Its *salts* are extremely soluble and mostly uncrystallisable. The *chloroplatinate* is deposited in the form of an oil which does not solidify. (Hofmann.)

## Biethaniline.

$$C^{20}NH^{15} = C^{12}(C^4H^5)^2NH^3,H^2.$$

A. W. Hofmann. (1850.) *Ann. Pharm.* 74, 135.

*Diethylaniline, Diethylophenylamine, Bivinanilin.—Formation* (p. 306).

*Preparation.* The crystals which separate from a mixture of ethaniline with a very large excess of bromide of ethyl, are freed from adhering bromide of ethyl, and treated with potash as in the preparation of ethaniline.

*Properties.* Transparent, colourless oil of sp. gr. 0·936 at 18°, boiling with perfect steadiness at 213·5°, and exhibiting with firwood and chloride of lime, the same reactions as ethaniline.

| | | | Hofmann. |
|---|---|---|---|
| 20 C | 120 | 80·54 | 80·76 |
| N | 14 | 9·39 | |
| 15 H | 15 | 10·07 | 10·22 |
| $C^{20}NH^{15}$ | 149 | 100·00 | |

$= C^{12}H^5(C^4H^5)^2,N.$ (Hofmann.)

The liquid remains transparent and colourless when exposed to the air.

It cannot be made to take up more $C^4H^5$ by heating it to 100° for several days in a sealed tube in contact with bromide of ethyl; only in presence of a trace of water crystals of hydrobromate of biethaniline are formed. With iodide of ethyl, a different action takes place. (*vid. inf.*)

*Hydrobromate of Biethaniline.* — *Preparation (vid. sup.)* — Large four-sided tables, which, at a gentle heat, melt and sublime in needles without decomposition; but when quickly heated are almost wholly resolved into an oily distillate consisting of ethaniline and bromide of ethyl. It contains 35·14 p. c. hydrobromic acid, and is therefore $C^{20}NH^{15},HBr$.

*Chloroplatinate of Biethaniline.* — Precipitated from somewhat concentrated solutions of hydrochlorate of biethaniline and bichloride of platinum, in the form of a brownish-yellow oil which soon solidifies in a hard mass; but from more dilute solutions it is gradually deposited in yellow prisms which may be purified by crystallisation from alcohol. Less soluble both in alcohol and in water than the platinum-salt of ethaniline. (Hofmann.)

| | | | Hofmann. |
|---|---|---|---|
| 20 C | 120·0 | 33·78 | 33·78 |
| N | 14·0 | 3·94 | |
| 16 H | 16·0 | 4·51 | 4·53 |
| Pt | 99·0 | 27·87 | 27·66 |
| 3 Cl | 106·2 | 29·90 | |
| $C^{20}NH^{15},HCl + PtCl^2$ | 355·2 | 100·00 | |

## Triethaniline.

$$C^{24}NH^{19} = C^{12}(C^4H^5)^3NH^3,H^2.$$

HOFMANN. *Ann. Pharm.* 79, 11; *Chem. Soc. Qu. J.* 4, 318.

*Trivinalin.* — Supposing it to contain 1 At. H more, it will be *Triethylophenyl-ammonium* [or *triethyphenylium*] $C^{12}H^5(C^4H^5)^3N$. (Hofmann.)
Known only as a hydrate and in combination with acids.

The clear mixture of biethaniline and iodide of ethyl enclosed in a sealed tube and heated for 12 hours in the water-bath, deposits a layer of hydriodate of triethaniline, which increases up to a certain point and solidifies on cooling in a soft crystalline mass. This product is freed from excess of iodide of ethyl or biethaniline by distillation, and then digested with silver-oxide and water, whereby it is converted into a bitter alkaline solution of triethaniline, which is separated by filtration from the iodide of silver and excess of oxide of silver, aggregated together by the biethaniline.

This solution, when evaporated, leaves the *Hydrate of Triethaniline* $C^{24}NH^{19},2HO$ ( = Hofmann's hydrated oxide of triethylophenyl-ammonium = $C^{12}H^5(C^4H^5)^3NO,HO$), which is resolved by distillation into water, olefiant gas and biethaniline:

$$C^{24}NH^{19},2HO = 2HO + C^4H^4 + C^{20}NH^{15}.$$

The compounds of triethaniline with sulphuric, hydrochloric, nitric and oxalic acid crystallise with tolerable facility. The hydrochlorate forms with bichloride of platinum a pale yellow amorphous precipitate, nearly insoluble in water, quite insoluble in alcohol and ether, and containing 25·77 p. c. platinum, therefore = $C^{24}NH^{19},HCl, PtCl^2$ ( = Hofmann's $C^{12}H^5(C^4H^5)^3NCl, PtCl^2$). Hofmann.

## Ethybromaniline.

$C^{16}NBrH^{10} = C^{12}(C^4H^5)NBrH^3,H^2.$

*Ethylobromaniline, Vinebromanilin.* — Bromaniline treated with excess of bromide of ethyl is quickly converted into hydrobromate of ethybromaniline (p. 278).

Ethybromaniline exactly resembles ethychloraniline.

Its platinum salt is a viscid oil. (Hofmann, *Ann. Pharm.* 74, 125.)

## Ethychloraniline.

$C^{16}NClH^{10} = C^{12}(C^4H^5)NClH^3,H^2.$

*Ethylochloraniline, Vinechloranilin.*— A mixture of chloraniline and excess of bromide of ethyl, kept for some days at 100°, and then freed from excess of bromide of ethyl by distillation with water, leaves a solution of hydrobromate of ethychloraniline, on which a few drops of the base float. This base is completely separated by potash in the form of an oil of high boiling point, remaining liquid below 0°, and having an odour like that of anise-oil.

The salts of this base are much more soluble than those of chloraniline.

The sulphate and oxalate crystallise; the chloroplatinate does not. (Hofmann, *Ann. Pharm.* 74, 143.)

## Biethychloraniline.

$C^{20}NClH^{14} = C^{12}(C^4H^5)^2NClH^2,H^2.$

*Diethylochloraniline, Bivinechloranilin.* — When a mixture of bromide of ethyl and ethychloraniline dried in a hot current of air, is heated to 100° for two days, it is converted into hydrobromate of biethychloraniline; and from this the base is separated by potash as a brownish oil, which is purified by solution in ether, freed from potash by washing with water, and from ether by evaporation.

The solution of the base in hydrochloric acid yields with bichloride of platinum, an orange-yellow crystalline precipitate, which, after washing with water, contains 24·53 p. c. platinum, and is therefore $C^{20}NClH^{14} + PtCl^2$. (Hofmann, *Ann. Pharm.* 74, 143.)

## Ethynitraniline.

$C^{16}N^2H^{10}O^4 = C^{12}(C^4H^5)NXH^3,H^2.$

*Ethylonitraniline, Vinenitranilin.*— From the large pale yellow crystals of hydrobromate of ethynitraniline obtained by the action of bromide of

ethyl on nitraniline, potash separates the alkaloid in the form of a yellowish-brown oil which solidifies after a while in the crystalline form, and separates from hot water in yellow stars.

It dissolves with tolerable facility in boiling water.

Its salts are colourless, have a sweet taste like those of nitraniline, dissolve in water as easily as the latter or even more easily, and do not crystallise till their solutions are evaporated nearly to dryness.

Ethynitraniline dissolved in not too large a quantity of strong hydrochloric acid, precipitates from bichloride of platinum crystalline scales which must be washed with cold water. They contain 26·23 p. c. platinum, and are therefore $C^{16}NXH^{10},HCl,PtCl^2$.

Ethynitraniline dissolves readily in alcohol and ether. (Hofmann, *Ann. Pharm.* 74, 146.)

## Oxanilic Acid.

$$C^{16}NH^7O^6 = C^{12}(C^4HO^2)AdH^4O^4.?$$

LAURENT & GERHARDT. (1848.) *N. Ann. Chim. Phys.* 24, 166; also *N. J. Pharm.* 14, 133.

*Preparation.* Aniline mixed with a very large excess of oxalic acid is fused for 10 minutes at a high temperature; the cooled mass boiled with water; and the solution filtered from the oxanilide; whereupon it yields, on cooling, crystals of bioxanilate of aniline, whilst a portion of the salt, together with a small quantity of formanilide and a large quantity of oxalic acid, remains in the mother-liquor, from which, by precipitation at a boiling heat with chloride of calcium, filtering while hot from the oxalate of lime, and cooling, an additional crop of crystals of oxanilate of lime may be obtained. The above-mentioned brown crystals, which cannot be decolorised by recrystallisation, are converted, either by boiling with baryta-water, or by solution in ammonia and precipitation with chloride of barium, into oxalate of baryta, which must be washed with cold water, and decomposed by boiling with an equivalent quantity of sulphuric acid (an excess decomposes the oxanilic acid), after which the filtrate deposits the oxanilic acid in crystals by evaporation,—or they may be converted into the lime-salt by solution in ammonia and precipitation with chloride of calcium, and that salt decomposed by sulphuric acid mixed with alcohol.

*Properties.* Beautiful laminæ, which redden litmus strongly.

| | *Crystals.* | | Laurent & Gerhardt. |
|---|---|---|---|
| 16 C | 96 | 58·18 | 58·2 |
| N | 14 | 8·48 | |
| 7 H | 7 | 4·24 | 4·3 |
| 6 O | 48 | 29·10 | |
| $C^{16}NH^7O^6$ | 165 | 100·00 | |

[= $C^{12}NH^7 + C^4H^2O^8 - 2HO = \left.\begin{matrix}N(C^{12}H^5)H(C^4O^4)\\ H\end{matrix}\right\}O^2$; that is to say, it may be regarded as hydrated oxide of ammonium, $\left.\begin{matrix}NH^4\\ H\end{matrix}\right\}O^2$, in which one of the hydrogen-atoms of the ammonium is replaced by phenyl and two others by the biatomic molecule $C^4O^4$. Gerhardt.)]

*Decompositions.* 1. Oxanilic acid, when heated, gives off carbonic oxide, carbonic acid and water, and is converted into pure oxanilide:

$$2C^{16}NH^7O^6 = C^{28}N^2H^{12}O^4 + 2CO + 2CO^2 + 2HO.$$

2. By boiling with dilute hydrochloric or sulphuric acid, it is resolved into hydrochlorate or sulphate of aniline, and free oxalic acid. — 3. With a boiling concentrated solution of potash it gives off aniline.

*Combinations.* The acid dissolves sparingly in cold, abundantly in hot *water.*

The *Oxanilates,* which are isomeric with the isatates, give off the whole of their aniline when heated with hydrate of potash, and a portion when boiled with potash-ley or strong acetic acid.

*Oxanilate of Ammonia.* — a. *Monobasic.* — Beautiful laminæ, which dissolve sparingly in cold, very easily in boiling water, and in alcohol. — *b. Bi-acid.* — The solution of the salt *a* is precipitated by hydrochloric acid, and the precipitate left to crystallise. Scales, sparingly soluble in cold water. — The salts *a* and *b* begin to decompose at 190°, give off ammonia, and afterwards carbonic oxide and carbonic acid together with a small quantity of aniline, and leave oxanilide.

| *a. Crystals.* | | | Laurent & Gerhardt. |
|---|---|---|---|
| 16 C | 96 | 52·75 | 52·65 |
| 10 H | 10 | 5·49 | 5·35 |
| 2 N6O | 76 | 41·76 | |
| $NH^3,C^{16}NH^7O^6$ | 182 | 100·00 | |

| *b. Crystals.* | | | Laurent & Gerhardt. |
|---|---|---|---|
| 32 C | 192 | 55·33 | 54·8 |
| 17 H | 17 | 4·90 | 5·0 |
| 3 N12O | 138 | 39·77 | |
| $NH^3,2C^{16}NH^7O^6$ | 347 | 100·00 | |

*Oxanilate of Baryta.* — The white crystalline precipitate, which the ammonia-salt forms with chloride of barium, crystallises from the solution in boiling water, in specular rhombic scales which contain 29·15 p.c. barium, and are therefore $C^{16}NH^6BaO^6$.

*Oxanilate of Lime.* — Obtained in a similar manner with chloride of calcium. Tufts of needles containing 10·8 p. c. calcium, therefore $C^{16}NH^6CaO^6$.

*Oxanilate of Silver.* — Obtained in like manner with nitrate of silver. White tabular crystals, which are nearly insoluble in cold, but dissolve

readily in hot water. They contain 39·8 p. c. silver, and are therefore $C^{16}NH^6AgO^6$.

*Oxanilate of Aniline.—Bi-acid.*—Prepared by the process given at page 310. Even after three recrystallisations, it forms dull brownish interlacing threads, which redden litmus, give off aniline when heated, and are then resolved, like the acid, into carbonic oxide, carbonic acid, water, and oxanilide; they separate unaltered from their solution in hydrochloric acid, and dissolve sparingly in cold, readily in hot water.

| | *Crystals.* | | Laurent & Gerhardt. |
|---|---|---|---|
| 44 C | 264 | 62·41 | 62·27 |
| 21 H | 21 | 4·97 | 4·97 |
| 3N12O | 138 | 32·62 | |
| $C^{12}NH^7,2C^{16}NH^7O^6$ | 423 | 100·00 | |

The acid dissolves very readily in *alcohol.* (Laurent & Gerhardt.)

## Oxanilamide.

$$C^{16}N^2H^8O^4 = C^{12}(C^4HO^2)Ad^2H^3,O^2.$$

A. W. Hofmann. (1850.) *Ann. Pharm.* 73, 181.

*Preparation.* A solution of cyaniline in dilute hydrochloric acid is evaporated; the white crystalline mass freed from sal-ammoniac and hydrochlorate of aniline by digestion in cold water; the residue well boiled with water; the solution evaporated to dryness after being filtered from the oxanilide; and the residue exhausted by boiling with alcohol. The alcoholic solution, when cooled or evaporated, deposits the oxanilamide, which may be purified by recrystallisation from hot water. The compound is not obtained by treating oxamethane ($C^8NH^7O^6$) with aniline.

*Properties.* Snow-white, silky, capillary flakes, which sublime in the form of a soft powder.

| | *Crystals.* | | Hofmann. |
|---|---|---|---|
| 16 C | 96 | 58·54 | 58·46 |
| 2 N | 28 | 17·07 | 16·71 |
| 8 H | 8 | 4·88 | 4·88 |
| 4 O | 32 | 19·51 | 19·95 |
| $C^{16}N^2H^8O^4$ | 164 | 100·00 | 100·00 |

*Decompositions.* 1. Oil of vitriol eliminates carbonic oxide and carbonic acid, and leaves sulphate of ammonia together with sulphanilic acid :

$$C^{16}N^2H^8O^4 + 3(HO,SO^3) = 2CO + 2CO^2 + C^{12}NH^7,2SO^3 + NH^4O,SO^3.$$

2. The originally transparent solution in strong potash-ley, from which acids thrown down the oxanilamide unaltered, becomes gradually

clouded with drops of aniline, the more quickly as it is stronger and warmer, then gives off ammonia, and forms oxalate of potash:

$$C^{16}N^2H^8O^4 + 2KO + 2HO = C^{12}NH^7 + NH^3 + C^4K^2O^8.$$

Continued boiling with water, or treatment with dilute acids or alkalis, does not decompose oxanilamide, not for example, into oxanilide and oxamide, as it might be supposed to do according to the equation: $C^{16}N^2H^8O^4 = C^{14}NH^6O^2$ (oxanilide) + $C^2NH^2O^2$ [or rather $C^4N^2H^4O^4$] (oxamide).

Oxanilamide is insoluble in water, but dissolves in ether and in strong alcohol. (Hofmann.)

## ¶. Amidonitroxanil.

$$C^{16}N^3H^5O^8 = C^{12}(C^4HO^2)NXAdH^2,O^2 ?$$

Gottlieb. *Ann. Pharm*, 85, 38.

*Oxalazophenylimide* (Gottlieb), *Nitrazophenyl-oximide* (Gerhardt.)

When amidonitraniline is dissolved in excess of oxalic acid and the liquid evaporated over the water-bath, a brownish-green residue is obtained, consisting partly of amidonitroxanilic acid and partly of amidonitroxanil; if kept for some time at 100°, it is almost wholly converted into the latter without change of aspect:

$$C^{12}N^3H^7O^4,C^4H^2O^8 - 2HO = \underbrace{C^{16}N^3H^7O^{10}}_{\text{amidonitroxanilic acid}};$$

and:

$$C^{16}N^3H^7O^{10} - 2HO = \underbrace{C^{16}N^3H^5O^8}_{\text{amidonitroxanil}}.$$

| | | | Gottlieb. |
|---|---|---|---|
| 16 C | 96 | 46·37 | 46·60 |
| 3 N | 42 | 20·29 | |
| 5 H | 5 | 2·42 | 2·65 |
| 8 O | 64 | 30·92 | |
| $C^{16}N^3H^5O^8$ | 207 | 100·00 | |

## ¶. Amidonitroxanilic Acid.

$$C^{16}N^3H^7O^{10} = C^{12}(C^4HO^2)NXAd^2H^2,O^4. ?$$

Gottlieb. *Ann. Pharm.* 85, 38.

*Oxalazophenylamic acid* (Gottlieb), *Nitrazophenyl-oxamic acid* (Gerhardt).

*Preparation* (*vid. sup.*) — May also be obtained by decomposing the baryta-salt with hydrochloric acid.

Small, light yellow, shining, granular crystals.

*Amidonitroxanilate of Ammonia* is obtained by treating the acid with aqueous ammonia. Yellow, sparingly soluble salt which crystallises from its hot aqueous solution in yellow needles.

*Amidonitroxanilate of Baryta* $C^{16}N^3H^6BaO^{10}$.—The ammonia-salt mixed with chloride of barium forms a light, orange-coloured, crystalline precipitate sparingly soluble in boiling water. The salt dried at 100° contains 3 At. water, which it gives off at 160°.

| *At* 160°. | | | Gottlieb. |
|---|---|---|---|
| $C^{16}N^3H^6O^9$ | 216·0 | 73·84 | |
| BaO | 76·6 | 26·16 | 26·39 |
| $C^{16}N^3H^6BaO^{10}$ | 292·6 | 100·00 | |

| *At* 100°. | | | Gottlieb. |
|---|---|---|---|
| $C^{16}N^3H^6O^9$ | 216·0 | 67·59 | |
| BaO | 76·6 | 23·96 | 24·22 |
| 3 HO | 27·0 | 8·45 | |
| $C^{16}N^3H^6BaO^{10}$ + 3Aq | 319·6 | 100·00 | |

## ¶. Acetanilide.

$$C^{16}NH^9O^2 = C^{12}(C^4H^3O^2)NH^4,H^2.$$

GERHARDT. *Ann. Pharm.* 87, 164.

*Formation and Preparation.* By the action of aniline upon chloride of acetyl or anhydrous acetic acid:

$$[C^4H^3O^2Cl + C^{12}NH^7 = C^{16}NH^9O^2 + HCl;$$

and:

$$C^4H^3O^3 + C^{12}NH^7 = C^{16}NH^9O^2 + HO.]$$

Chloride of acetyl dropped into aniline produces a hissing noise like the quenching of red-hot iron, and the mixture solidifies on cooling in a crystalline mass which may be washed with cold water to remove hydrochlorate of aniline, and recrystallised from boiling alcohol; the solution on cooling deposits the acetanilide in splendid laminæ. If impure aniline is used in the preparation, the crystals have generally a reddish colour, which however may be removed by leaving them to dry, dissolving in boiling water, and filtering; a small quantity of brown oily matter then remains on the filter.—Acetanilide may be obtained in exactly the same manner from anhydrous acetic acid. Colourless shining laminæ which melt at 112° and solidify in a crystalline mass on cooling. The compound distils without decompostion. Boiling potash-ley has scarcely any action upon it, but fused hydrate of potash immediately eliminates aniline.

| | | | | | |
|---|---|---|---|---|---|
| | | | | | Gerhardt. |
| 16 C | 96 | .... | 71·11 | ........ | 71·22 |
| N | 14 | .... | 10·37 | ........ | 10·84 |
| 9 H | 9 | .... | 6·66 | ........ | 6·77 |
| 2 O | 16 | .... | 11·86 | ........ | 11·17 |
| $C^{16}NH^9O^2$ | 135 | .... | 100·00 | ........ | 100·00 |

$= N(C^{12}H^5)H(C^4H^3O^2)$.

Acetanilide dissolves sparingly in cold water, but with tolerable facility in hot water, in alcohol and in ether. (Gerhardt.) ¶.

## Oxaluranilide.

$C^{18}N^3H^9O^6 = C^{12}(C^6HO^4)Ad^3H^2,O^2$.

LAURENT & GERHARDT (1848). *N. Ann. Chim. Phys.* 24, 177.

*Preparation.* 1. Finely pulverised parabanic acid mixed and heated with anhydrous aniline, solidifies, without evolution of water, in the form of crystalline oxaluranilide, which is freed from excess of parabanic acid or of aniline by boiling with a large quantity of alcohol, and then washed and dried:

$$C^{12}NH^7 + C^6N^2H^2O^6 = C^{18}N^3H^9O^6.$$

2. The same body quickly crystallises from a solution of aniline in boiling aqueous parabanic acid.

*Properties.* White crystalline powder having a somewhat pearly lustre, and appearing needle-shaped under the microscope; melts at a strong heat; destitute of taste and odour.

| | | | | | |
|---|---|---|---|---|---|
| | | | | | Laurent & Gerhardt. |
| 18 C | 108 | .... | 52·17 | ........ | 52·1 |
| 3 N | 42 | .... | 20·29 | | |
| 9 H | 9 | .... | 4·35 | ........ | 4·3 |
| 6 O | 48 | .... | 23·19 | | |
| $C^{18}N^3H^9O^6$ | 207 | .... | 100·00 | | |

*Decompositions.* 1. Heated above its melting point, it gives off very acrid vapours containing cyanogen.—2. Its solution in oil of vitriol when heated gives off carbonic oxide and carbonic acid without blackening, while sulphate of ammonia and sulphanilic acid remain. In this case, oxalic acid and urea are formed from the parabanic acid residue, the former yielding carbonic oxide and carbonic acid, and the latter carbonic acid and ammonia:

$$C^{18}N^3H^9O^6 + 4HO + 6SO^3 = C^{12}NH^7,2SO^3 + 2CO + 4CO^2 + 2NH^3,4SO^3.$$

3. Heated with hydrate of potash, it yields aniline and ammonia.

Oxaluranilide is insoluble in water, and very sparingly soluble in boiling alcohol. (Laurent & Gerhardt.)

## ¶. Butyranilide.

$$C^{20}NH^{13}O^2 = C^{12}(C^8H^7O^2)NH^4,H^2. ?$$

GERHARDT. *Ann. Pharm.* 87, 166.

Obtained by the action of aniline on anhydrous butyric acid or chloride of butyral. When aniline is brought in contact with a mixture of these two substances, heat is evolved, and the product solidifies on cooling. If water acidulated with hydrochloric acid be then poured upon it to remove the excess of aniline, the butyranilide separates in the form of an oil which is generally coloured and often remains liquid for a day or two, but solidifies when briskly agitated. From a solution in boiling dilute alcohol it separates in the crystalline state.

Beautiful nacreous laminæ, which melt at 90°, and distil over undecomposed. Boiling potash-ley has scarcely any action upon the compound, but fused hydrate of potash eliminates aniline.

| | *Crystals.* | | Gerhardt. |
|---|---|---|---|
| 20 C | 120 | 73·62 | 73·56 |
| N | 14 | 8·58 | 8·80 |
| 13 H | 13 | 7·96 | 8·06 |
| 2 O | 16 | 9 84 | 9·58 |
| $C^{20}NH^{13}O^2$ | 163 | 100·00 | 100·00 |

$$= C^{12}NH^7 + C^8H^8O^4 - 2HO = N(C^{12}H^5)H(C^8H^7O^2).$$

Insoluble in water, readily soluble in alcohol and ether. (Gerhardt.) ¶.

## Succinanil.

$$C^{20}NH^9O^4 = C^{12}(C^8H^5O^2)NH^4,O^2. ?$$

LAURENT & GERHARDT. (1848.) *N. Ann. Chim. Phys.* 24, 179.

Formed, together with succinanilide, on melting succinic acid with excess of aniline, and extracted from the fused mass by boiling water from which it separates on cooling; it may then be crystallised from alcohol.

Long interlaced needles, which melt at 158° and solidify in a radiated mass on cooling; may be sublimed without decomposition.

| | | | Laurent & Gerhardt. |
|---|---|---|---|
| 20 C | 120 | 68·57 | 68·6 |
| N | 14 | 8·00 | |
| 9 H | 9 | 5·14 | 5·3 |
| 4 O | 32 | 18·29 | |
| $C^{20}NH^9O^4$ | 175 | 100·00 | |

$$[= C^{12}NH^7 + C^8H^6O^8 - 4HO = N\left\{\begin{matrix} C^8H^4O^4 \\ C^{12}H^5 \end{matrix}\right. .]$$

Dissolves in boiling aqueous potash in the form of succinanilic acid, by taking up 2HO; with hydrate of potash it immediately gives off aniline.

Dissolves readily in water, hydrochloric acid, nitric acid, alcohol and ether. (Laurent & Gerhardt.)

## Succinanilic Acid.

$$C^{20}NH^{11}O^{4} = C^{12}(C^{8}H^{5}O^{2})AdH^{4},O^{4}. ?$$

LAURENT & GERHARDT. (1848). *N. Ann. Chim. Phys.* 24, 180.

*Preparation.* Succinanil is dissolved in boiling dilute ammonia mixed with a little alcohol; the liquid boiled till the alcohol evaporates; then neutralised with nitric acid; and the crystals which form on cooling, purified by crystallisation from alcohol.

*Properties.* Elongated crystalline laminæ, which melt at 155°, and on cooling solidify in a crystalline mass (not radiated); they redden litmus.

| *Crystals.* | | | Laurent & Gerhardt. |
|---|---|---|---|
| 20 C | 120 | 62·18 | 62·15 |
| N | 14 | 7·25 | |
| 11 H | 11 | 5·70 | 5·85 |
| 6 O | 48 | 24·87 | |
| $C^{20}NH^{11}O^{6}$ | 193 | 100·00 | |

$$[= C^{12}NH^{7} + C^{8}H^{6}O^{8} - 2HO = \left\{\begin{matrix} N(C^{12}H^{5})H(C^{8}H^{4}O^{4} \\ H \end{matrix}\right\} O^{2}.]$$

*Decompositions.* 1. The acid heated above its melting point is resolved into water and a sublimate of succinanil. — 2. When fused at a gentle heat with hydrate of potash, it gives off aniline.

*Combinations.* The acid dissolves very sparingly in cold, more freely in hot *water.*

From the aqueous solutions of the *Succinanilates,* mineral acids precipitate succinanilic acid in the crystalline form.

*Succinanilate of Ammonia.*—Entangled crystals, soluble with tolerable facility in water.

The acid dissolves in *potash.* The ammonia-salt does not precipitate *chloride of calcium,* and forms only with a concentrated solution of *chloride of barium,* a slight precipitate which dissolves readily in hot water. With *ferrous salts* it forms a yellowish-white, sparingly soluble precipitate; with *cupric* sulphate, a light blue insoluble precipitate; and with nitrate of *silver,* a white, likewise insoluble precipitate, which contains 36·2 p. c. silver, and is therefore $C^{20}NH^{10}AgO^{6}$.

The acid dissolves very readily in *alcohol* and *ether,* and crystallises therefrom. (Laurent & Gerhardt.)

## ¶. Sulphosuccinanil.

$$C^{20}NH^9S^2O^8 = C^{12}(C^8H^5S^2O^6)NH^4,O^2. ?$$

GERHARDT & CHIOZZA. (1853.) *N. Ann. Chim. Phys.* 47, 129.

*Sulphophenyl-succinamide, Azoture de Sulphophényle et de Succinyle.*

Obtained by the action of chloride of succinyl on sulphophenylamide (p. 237.)

$$[C^{12}NH^7S^2O^4 + C^8H^4O^4Cl^2 = C^{20}NH^9S^2O^8 + 2HCl.)$$

The action begins at 125°; a copious evolution of hydrochloric acid takes place between 125° and 145°, but soon ceases altogether and the mixture solidifies; between 160° and 200°, it melts again and gives off more hydrochloric acid. When the action is complete, the product remains viscid for a long time, but ultimately aggregates into a crystalline mass: the addition of alcohol causes it to solidify immediately.

Deposited from boiling water in snow-white crystals; from the alcoholic solution, sometimes in splendid needles several centimetres long, sometimes in shortened prisms; sometimes both these forms appear together, passing indeed one into the other when the mixture is agitated. Melts at about 160°, and when more strongly heated in a small retort, it is decomposed, with formation of sulphurous acid, and of certain oils which partly solidify on cooling: cyanide of phenyl does not occur among the products of the decomposition.

| | | |
|---|---|---|
| 22 C | 132 | 52·60 |
| N | 14 | 5·58 |
| 9 H | 9 | 3·57 |
| 2 S | 32 | 12·75 |
| 8 O | 64 | 25·50 |
| $C^{22}NH^9S^2O^8$ | 251 | 100·00 |

$$= N(C^{12}H^5S^2O^4)(C^8H^4O^4).$$

Dissolves sparingly in boiling *water;* dissolves also in *ammonia* but not immediately; sparingly also in *alcohol* and *ether.*

## ¶. Sulphosuccinanilic Acid.

$$C^{20}NH^{11}S^2O^{10} = C^{12}(C^8H^5S^2O^6)AdH^4,O^4. ?$$

GERHARDT & CHIOZZA. (1853). *N. Ann. Chim. Phys.* 47, 129.

*Acide phenyl-succinamique.*

Obtained as an ammonia-salt by dissolving sulphosuccinanil in strong ammonia, and evaporating the solution, first at a gentle heat, afterwards in vacuo. A thick syrup is then left, which ultimately solidifies in con-

centric silky fibres. Crude sulphosuccinanil may be used in the preparation; for when it is dissolved in ammonia, the impurities soon separate, and a colourless solution is obtained.

The *Ammonia-salt* melts at 165°, giving off a large quantity of ammonia, and an oil is obtained which, when dissolved in boiling water, yields crystals of sulphophenylamide. It is very soluble in water; dissolves also in alcohol.

| | | | | | Gerhardt & Chiozza. |
|---|---|---|---|---|---|
| 20 C | 120 | .... | 43·80 | ........ | 44·1 |
| 2 N | 28 | .... | 10·22 | ........ | 10·3 |
| 14 H | 14 | .... | 5·11 | ........ | 5·2 |
| 2 S | 32 | .... | 11·67 | | |
| 10 O | 80 | .... | 29·20 | | |
| $C^{20}N^2H^{10}(NH^4)S^2O^8$ | 274 | .... | 100·00 | | |

The aqueous solution of this salt treated with a few drops of hydrochloric acid, yields splendid needles, which melt between 155° and 160°, but have exactly the same composition as the original salt.

The *Silver-salt* $C^{20}NH^{10}AgO^{10}$, is deposited on adding nitrate of silver to a solution of the ammonia-salt, in beautiful needles containing 28·7 p.c. silver. (Gerhardt & Chiozza.)

## ¶. Malanil.

$$C^{20}NH^9O^6 = C^{12}(C^8H^5O^4)NH^4,O^2. ?$$

E. Arppe. *Ann. Pharm.* 96, 106.

*Phenyl-malimide, Nitride of Phenyl and Malyl.*

Formed, together with malanilide $C^{32}N^2H^{16}O^6$, by melting a mixture of malic acid and aniline:

$$C^{12}NH^7 + C^8H^6O^{10} - 4HO = C^{20}NH^9O^6;$$

and:

$$2C^{12}NH^7 + C^8H^6O^{10} - 4HO = C^{32}N^2H^{16}O^6.$$

When the fused mixture is kept in a state of gentle ebullition for about two hours, a brown syrup is obtained, which solidifies on cooling, and when boiled with water, yields a nearly colourless solution of malanil and a coloured residue containing malanilide. The solution when evaporated yields malanil in the form of a granular mass, still however mixed with malanilide, from which it is purified by digestion in hot water and filtration. The solution is then further purified by treatment with animal charcoal, and evaporated to the crystallising point.

From a hot concentrated aqueous solution, malanil separates on cooling in delicate needles grouped together; also when its alcoholic solution is evaporated; sometimes however it forms nacreous laminæ, and from a very dilute aqueous solution, it is deposited in very thin iridescent rectangular prisms. Melts at 170°, and when heated between two watch-glasses, forms a slight mealy sublimate.

| | | | | | Arppe. |
|---|---|---|---|---|---|
| 20 C | 120 | .... | 62·83 | ........ | 62·80 |
| N | 14 | .... | 7·33 | | |
| 9 H | 9 | .... | 4·71 | ........ | 4·77 |
| 6 O | 48 | .... | 25·13 | | |
| $C^{20}NH^9O^6$ | 201 | .... | 100·00 | | |

$$[= C^{12}NH^7 + C^8H^6O^{10} - 4HO \quad N\left\{\begin{matrix} C^8H^4O^6 \\ C^{12}H^5 \end{matrix}\right].$$

Malanil boiled with aqueous ammonia is converted into malanilate of ammonia.

It dissolves easily in the strongest nitric acid, forming a deep red solution, from which water throws down a nearly colourless, indistinctly crystalline body, probably nitromalanil, accompanied by a resinous body which is very difficult to separate. The crystalline body dissolves easily in boiling water, and the solution on cooling yields fine needles.

Malanil dissolves very abundantly in *water, alcohol,* and *ether.* (Arppe.)

## ¶. Malanilic Acid.

$$C^{20}NH^{11}O^8 = C^{12}(C^8H^5O^4)AdH^4,O^4. ?$$

ARPPE. *Ann. Pharm.*. 96, 111.

*Phenyl-malamic acid.*

Obtained in the form of an ammonia-salt by boiling malanil with aqueous ammonia (*vid. sup.*) The solution of this salt forms with baryta a copious precipitate, which, when mixed with a small quantity of water, and decomposed, with the aid of heat, by an exactly equivalent quantity of sulphuric acid, yields malanilic acid; and from the solution filtered while yet warm, the acid crystallises on cooling and may be purified by recrystallisation from alcohol. The slightest excess of sulphuric acid used in the preparation converts the malanilic acid into malanil; hence it is best to use rather less than the equivalent quantity.

Crystallises in white, faintly lustrous granules, composed of very minute needles, and scarcely attaining the size of a pin's head. Melts at 145°. Has a very sour taste, reddens litmus, and decomposes carbonates. Dissolves readily in water. Its salts are also distinguished by their solubility in water.

The solution of the *Ammonia-salt* remains clear when mixed with *lime-water,* but is slightly clouded by boiling with *potash;* with acetate of *lead,* it forms a white precipitate soluble in water; and with *sesqui-chloride of iron* a precipitate of a fine yellow colour.

The *Baryta-salt* is very soluble in water and crystallises in spherical nodules of a dazzling whiteness; it is insoluble in hydrochlorate of ammonia.

*Malanilate of Silver* $C^{20}NH^{10}AgO^8$, forms a white pcecipitate which soon becomes coloured by exposure to light; it dissolves in water, and

is deposited from the solution in brilliant scales. Contains 34·19 p.c. silver.

Malanilic acid dissolves in *alcohol*, and sparingly in *ether*. (Arppe.)

## ¶. Citraconanil.

$C^{22}NH^9O^4 = C^{12}(C^{10}H^5O^2)NH^4,O^2$. ?

GOTTLIEB. *Ann. Pharm.* 77, 277.

*Phenyl-citraconimide, Nitride of Phenyl and Citraconyl.*

*Preparation.*—1. By mixing anhydrous citraconic acid with aniline. The mixture becomes very hot, and if kept for some time at the temperature of the water-bath, solidifies into a mass of crystals of citraconanil.—2. By boiling or concentrating over the water-bath, an aqueous solution of citraconic acid mixed with aniline. The tendency of citraconic acid in presence of aniline to form this body, is so great, that citraconate of aniline cannot be obtained by adding aniline to a solution of citraconic acid or of acid citraconate of ammonia.—3. By distilling a mixture of aniline and mesaconic acid.—4. By the action of heat on citraconanilic acid.—The compound obtained by either of these processes, is contaminated with a small quantity of a pitchy substance from which it may be purified by crystallisation from boiling water.

*Properties.*—Crystallises from its aqueous solution in shining needles, which, when they separate from a dilute solution, are often an inch in length: they are brittle and easily pulverised; inodorous. The compound melts at 96°, forming a colourless oil which sinks in boiling water. Heated above 100°, it volatilises readily, and in small quantities may be sublimed without decomposition, being then deposited on the sides of the vessel in colourless crystals. When slowly evaporated, it exhales a faint odour of roses; but larger quantities of the vapour have a sharp odour which excites coughing. The boiling aqueous solution also exhales an odour of roses, mixed however with that of aniline, which indicates a slight decomposition; from the same cause, a slip of firwood immersed in the solution acquires a yellow colour. The solutions of citraconil are not altered by chloride of lime.

| | | | Gottlieb. |
|---|---|---|---|
| 22 C | 132 | 70·58 | 70·45 |
| N | 14 | 7·48 | 7·69 |
| 9 H | 9 | 4·82 | 4·91 |
| 4 O | 32 | 17·12 | 16·95 |
| $C^{22}NH^9O^4$ | 187 | 100·00 | 100·00 |

$= C^{22}NH^7 + C^{10}H^6O^8 - 4HO$; may be regarded as $N\left\{\begin{matrix}C^{10}H^4O^4\\C^{12}H^5\end{matrix}\right.$ that is, as ammonia in which 2 At H are replaced by the biatomic radical $C^{10}H^4O^4$ citraconyl, and the third by phenyl.

Citraconanil is sparingly soluble in *water*.

Dissolves in *oil of vitriol* at ordinary temperatures, forming a red-brown solution, from which it is precipitated by water without alteration.

Dissolves readily in *alcohol* and *ether*. (Gottlieb.)

## ¶. Citraconiodanil.

$$C^{22}NIH^8O^4 = C^{12}(C^{10}H^5O^2)NIH^3,O^2. ?$$

GOTTLIEB. *Ann. Pharm.* 77, 289.

*Iodophenyl-citraconimide.*

Obtained by boiling iodaniline with water and excess of citraconic acid. Purified by crystallisation from boiling water.

Crystallises in slender needles resembling those of citraconanil, but smaller and having a slight yellowish tinge. When heated, it melts and decomposes, giving off vapours of iodine; a portion, however, appears to sublime unaltered.

| | | | Gottlieb. |
|---|---|---|---|
| 22 C | 132 | 42·31 | 42·04 |
| N | 14 | 4·49 | |
| 8 H | 8 | 2·56 | 2·82 |
| I | 126 | 40·38 | |
| 4 O | 32 | 10·26 | |
| $C^{22}NIH^8O^4$ | 312 | 100·00 | |

May be regarded as $N\left\{\begin{array}{l}C^{10}H^4O^4\\C^{12}IH^4\end{array}\right.$

Dissolves sparingly in *water*, abundantly in *alcohol*. (Gottlieb.)

## ¶. Citracobinitranil.

$$C^{22}N^3H^7O^{12} = C^{12}(C^{10}H^5O^2)NX^2H^2,O^2. ?$$

GOTTLIEB. *Ann. Pharm.* 85, 21.

*Citracondinitranil, Dinitrophenyl-citraconimide.*

Obtained by introducing citraconanil in successive small portions into a mixture of nitric acid and oil of vitriol, immersed in ice to moderate the action, which would otherwise be too violent, and give rise to the formation of a resinous product. The solution is then poured into ice-cold water, and the precipitated citracobinitranil washed with water, dissolved in boiling alcohol, and purified by recrystallisation with the aid of animal charcoal.

Colourless needles united in concentric groups. Melts when heated, and decomposes with a slight explosion.

| | | | | | | Gottlieb. |
|---|---|---|---|---|---|---|
| 22 C | 132 | .... | 47·65 | | ........ | 47·57 |
| 3 N | 42 | .... | 15·16 | | ........ | 15·05 |
| 7 H | 7 | .... | 2·53 | | ........ | 2·54 |
| 12 O | 96 | .... | 34·66 | | ........ | 34·84 |
| $C^{22}N^3H^7O^{12}$ | 277 | .... | 100·00 | | ........ | 100·00 |

May be regarded as $N\begin{cases} C^{10}H^4O^4 \\ C^{12}X^2H^3 \end{cases}$

The compound is not attacked by acids; but alkaline carbonates decompose it, producing, first an alkaline citracobinitranilate, and afterwards binitraniline (p. 292), and an alkaline citraconate.

Dissolves very sparingly in *water*, but abundantly in *alcohol*, especially when hot. (Gottlieb.)

## ¶. Citraconanilic Acid.

$$C^{22}NH^{11}O^6 = C^{12}(C^{10}H^5O^2)AdH^4,O^4. ?$$

GOTTLIEB. *Ann. Pharm.* 77, 280.

*Acide phényl-citraconamique.*

Obtained in the form of an ammonia-salt by boiling citraconanil with dilute ammonia for about a quarter of an hour. If the boiling be stopped before that time, the conversion is incomplete; if it be continued much longer, the acid is resolved into citraconic acid and aniline. When the action is supposed to be complete, the liquid is supersaturated with acetic acid, whereby the citraconanilic acid is separated as a crystalline precipitate, which is washed with cold water and recrystallised from a hot mixture of equal parts of ether and 80 per cent. alcohol. The first crystals deposited from this solution consist of pure citraconanilic acid; the remainder are contaminated with citraconanil.

Small shining crystals, whose solution has an acid reaction.

| | | | | | Gottlieb. |
|---|---|---|---|---|---|
| 22 C | 132 | .... | 64·39 | ........ | 64·40 |
| N | 14 | .... | 6·83 | | |
| 11 H | 11 | .... | 5·36 | ........ | 5·54 |
| 6 O | 48 | .... | 23·42 | | |
| $C^{22}NH^{11}O^6$ | 205 | .... | 100·00 | | |

$$[= C^{12}NH^7 + C^{10}H^6O^8 - 2HO = \left.\begin{matrix} N(C^{12}H^5),H,(C^{10}H^4O^4) \\ H \end{matrix}\right\}O^2.]$$

The acid is very instable; when melted, it is resolved into water and citraconanil.

Heated with water and carbonate of *baryta,* it yields nothing but citraconate of baryta.

When saturated with ammonia and treated with nitrate of *silver,* it yields a white precipitate, which blackens when boiled with water, forming a red solution which deposits citraconate of silver.

The acid dissolves sparingly in *water,* readily in *alcohol.* (Gottlieb.)

## ¶. Itaconanilic Acid.

$$C^{22}NH^{11}O^6 = C^{12}(C^{10}H^5O^2)AdH^4,O^4. ?$$

GOTTLIEB. *Ann. Pharm.* 77, 284.

*Acide phényl-itaconamique.*

Obtained by mixing aniline with excess of aqueous itaconic acid, evaporating to dryness, heating the residue a little above 100°, and crystallising from boiling water. The whole of the aniline is thus transformed into itaconanilic acid.

Crystallises from the hot aqueous solution in brown shining needles; from alcohol in groups of tabular crystals. Melts at 189° with partial decomposition, but is much more stable than citraconanilic acid. At 260° it is for the most part resolved into water, citraconanil, citraconic acid, itaconanilide, and itaconic acid, the two latter products remaining in the residue, while the others distil over. Neither the acid nor its salts is coloured by chloride of lime.

| | | | Gottlieb. |
|---|---|---|---|
| 22 C | 132 | 64·39 | 64·35 |
| N | 14 | 6·83 | |
| 11 H | 11 | 5·36 | 5·33 |
| 6 O | 48 | 23·42 | |
| $C^{22}NH^{11}O^6$ | 205 | 100·00 | |

The acid dissolves in *water.*

Its *salts,* whose general formula is $C^{22}NH^{10}MO^6$, are much more stable than those of citraconanilic acid; but nevertheless are slightly decomposed when their solutions are boiled. Mineral acids added to these solutions separate the itaconanilic acid in the form of a white crystalline precipitate.

An *acid ammonia-salt* is obtained as a sparingly soluble residue by evaporating a solution of the acid saturated with ammonia. It separates from a hot aqueous solution in small crystalline groups.

The *soda-salt* is obtained by saturating the acid with carbonate of soda. It dissolves very readily in water, and the solution yields by evaporation a syrupy liquid, whose surface after a while becomes covered with a crystalline crust.

*Itaconanilate of Baryta.* $C^{22}NH^{10}BaO^6$. — Obtained by boiling the acid with water and carbonate of baryta. The solution, when eva-

porated, yields a transparent, colourless, gummy mass, which exhibits no trace of crystallisation, even after a considerable time. The salt is very soluble in water. Dried at 170°, it contains 28·08 p. c. baryta.

*Itaconanilate of Lead* forms a white curdy precipitate, resembling chloride of lead; when left for some time in the liquid, it arranges itself in beautiful crystalline geodes.

*Itaconanilate of Copper*, $C^{22}NH^{10}CuO^6$, is obtained by mixing the solution of the soda-salt with sulphate of copper, in the form of a pale blue crystalline precipitate containing water, which it gives off only at a high temperature. At 160°, the salt assumes a bright bluish green colour, and is then found to contain 16·84 p.c. of cupric oxide.

*Itaconanilate of Silver.* — White crystalline precipitate, which dissolves in boiling water somewhat copiously, though with slight reduction, and crystallises on cooling in broad shining needles.

| | | | Gottlieb. |
|---|---|---|---|
| 22 C | 132 | 42·31 | 42·47 |
| N | 14 | 4·48 | |
| 10 H | 10 | 3·21 | 3·37 |
| Ag | 108 | 34·61 | 34·80 |
| 6 O | 48 | 15·39 | |
| $C^{22}NH^{10}AgO^6$ | 312 | 100·00 | |

By repeated crystallisation, this salt suffers a peculiar alteration, being converted into porcelain-like granules of another salt which has not been further examined.

The acid dissolves in *alcohol* more freely than in water.

## ¶. Citracobinitranilic Acid.

$$C^{22}N^3H^9O^{14} = C^{12}(C^{10}H^5O^2)AdX^2H^2,O^4. ?$$

GOTTLIEB. *Ann Pharm.* 85, 24.

*Citracondinitranilsäure, Acide dinitrophenyl-citraconamique.*

Obtained as a soda-salt by boiling citracobinitranil with a dilute solution of carbonate of soda, care being taken not to continue the ebullition too long, because the anil would then be resolved into binitraniline and citraconic acid (p. 323). On adding hydrochloric acid to the liquid after cooling, citracobinitranilic acid separates in the form of a yellow crystalline precipitate, which, when several times recrystallised from alcohol, forms broad, nearly colourless needles, contaminated however with a dark yellow substance which is very difficult to separate.

*Silver-salt.* $C^{22}N^3H^8AgO^{14}$. — Precipitated on adding nitrate of silver to a solution of the acid neutralised with ammonia, in the form of a pale yellow precipitate composed of crystalline scales. When dried in vacuo over oil of vitriol, it contains 27·60 p. c. silver, the formula requiring 26·86 p. c. (Gottlieb.)

## ¶. Amidonitrocitraconanil.

$$C^{22}N^3H^9O^8 = C^{12}(C^{10}H^5O^2)NXAdH^2,O^2. ?$$

GOTTLIEB. *Ann. Pharm.* 85, 36

*Citraconazophenylimide.*

Formed, together with a small quantity of amidonitrocitraconanilic acid, when a solution of amidonitraniline in excess of aqueous citraconic acid is evaporated over the water-bath. A crystalline, sparingly soluble residue is then obtained which consists chiefly of amidonitrocitraconanil, and may be freed from adhering acid by washing, first with water and then with dilute ammonia. The residue dissolved in alcohol yields the compound, on cooling, in slender, loose, needle-shaped, sulphur-yellow crystals, which may be purified by recrystallisation from alcohol.

| *Dried at* 100°. | | | Gottlieb. |
|---|---|---|---|
| 22 C | 132 | 53·44 | 53·48 |
| 3 N | 42 | 17·00 | 16·94 |
| 9 H | 9 | 3·64 | 3·75 |
| 8 O | 64 | 25·92 | 25·83 |
| $C^{22}N^3H^9O^8$ | 247 | 100·00 | 100·00 |

This compound melts when somewhat strongly heated, and decomposes quickly at a few degrees above its melting point, giving off acid vapours and leaving a carbonaceous mass. The fixed alkalis decompose it slowly. Ammonia dissolves it at the boiling heat, and acids added to the solution after cooling separate crystals, which appear to consist of the original compound.

It dissolves with tolerable facility in *alcohol* and *ether*. (Gottlieb.)

## ¶. Pyrotartanil.

$$C^{22}NH^{11}O^4 = C^{12}(C^{10}H^7O^2)NH^4,O^2?$$

ARPPE. *Ann. Pharm.* 90, 138.

*Pyrotartranil, Phenyl-pyrotartrimide, Nitride of Phenyl and Pyrotartryl.*

*Preparation.* When crystallised pyrotartaric acid is fused with aniline, and the mixture kept for about ten minutes at a temperature a few degrees above that of boiling water, a thick brown viscid mass is obtained, consisting chiefly of pyrotartanil, which solidifies gradually on agitation. It is dissolved in boiling water, best with addition of alcohol, the solution treated with animal charcoal, and then left to crystallise.

*Properties.* Pulverulent crystalline precipitate composed of microscopic needles. It is tasteless and inodorous. Melts at 98°, and when

immersed in boiling water, is converted into an oil which solidifies on cooling, in a crystalline mass unctuous to the touch. Volatilises without decomposition and sublimes with tolerable rapidity at 140°, but does not boil till it is heated to about 300°, at which temperature it suffers partial decomposition, but sublimes for the most part unaltered. — Very impure pyrotartanil may thus be purified by slow distillation.

| | | | Arppe. |
|---|---|---|---|
| 22 C | 132 | 69·84 | 69·81 |
| N | 14 | 7·41 | |
| 11 H | 11 | 5·82 | 5·92 |
| 4 O | 32 | 16·93 | |
| $C^{22}NH^{11}O^4$ | 189 | 100·00 | |

$$[= C^{12}NH^7 + C^{10}H^8O^8 - 4HO = N \begin{Bmatrix} C^{10}H^6O^2 \\ C^{12}H^5 \end{Bmatrix}.]$$

Strong *nitric acid* converts it into pyrotartonitranil.

It dissolves in cold aqueous *alkalis* without alteration, but when heated is converted into pyrotartanilic acid. By fusion with hydrate of potash or soda, it is resolved into aniline and pyrotartaric acid.

Dissolves but sparingly in *water*, even at the boiling heat, but readily in *alcohol* and *ether*. The addition of alcohol greatly increases the solvent power of water for this compound, without preventing its separation as the liquid cools. (Arppe.)

## ¶. Pyrotartonitranil.

$$C^{22}N^2H^{10}O^8 = C^{22}(C^{10}H^7O^2)NXH^3,O^2. ?$$

Arppe. *Ann. Pharm.* 90, 144.

*Pyrotartronitranil, Nitrophényl-pyrotartrimide.*

Obtained by dissolving pyrotartanil in very strong nitric acid and precipitating by water. It then separates in the form of an oil, which gradually solidifies and may be purified by crystallisation from boiling alcohol.

Long needles united in spherical groups. Melts at 155°, and solidifies in a crystalline mass at 153°. Volatilises without decomposition when carefully heated.

| | | | Arppe. |
|---|---|---|---|
| 22 C | 132 | 56·41 | 56·35 |
| 2 N | 28 | 11·97 | |
| 10 H | 10 | 4·27 | 4·34 |
| 8 O | 64 | 27·35 | |
| $C^{22}N^2H^{10}O^8$ | 234 | 100·00 | |

The compound when boiled with *ammonia* is converted into pyrotartronitanilic acid; the same product is formed by the action of the fixed alkalis, but is then further readily transformed into $\beta$-nitraniline (p. 288).

Nearly insoluble in water, but dissolves in *alcohol* and *ether*. (Arppe.)

## ¶. Pyrotartanilic Acid.

$$C^{22}NH^{13}O^6 = C^{12}(C^{10}H^7O^2)AdH^4,O^4. ?$$

ARPPE. *Ann. Pharm.* 90, 141.

*Pyrotartranilic acid, Acide phenyl-pyrotartramiqué.*

*Formation.* 1. By the action of aniline on anhydrous pyrotartaric acid. — 2. By the action of aqueous fixed alkalis on pyrotartanil.

*Preparation.* — When aniline is added by drops to anhydrous pyrotartaric acid (the watery oil obtained by distilling the hydrated acid may be used for the purpose), the mixture becomes hot, and solidifies in a crystalline pulp, which, when sufficient aniline has been added, breaks up and becomes nearly dry. It may be purified by solution in 20 or 24 parts of boiling water, or better in aqueous alcohol, with addition of animal charcoal.

*Properties.* Bulky crystalline mass, consisting of shining crystalline needles, which, when they separate from a somewhat dilute solution, are arranged in stellate groups, and appear under the microscope to have the form of rectangular prisms with the terminal faces perpendicularly set. May be heated to 140° without loss of weight; melts at 147°, giving off water at the same time, and being partially converted into the more fusible pyrotartanil; hence the acid, after being once fused, melts at 140°. It is very permanent and reddens litmus paper. Does not give the reaction of aniline with solution of chloride of lime. It is decomposed by an excess of boiling potash-ley.

| | | | Arppe. | |
|---|---|---|---|---|
| 22 C | 132 | 63·77 | 63·84 | 63·60 |
| N | 14 | 6·76 | | |
| 13 H | 13 | 6·28 | 6·54 | 6·32 |
| 6 O | 48 | 23·19 | | |
| $C^{22}NH^{13}O^6$ | 207 | 100·00 | | |

$$\left[= C^{12}NH^7 + C^{10}H^8O^8 - 2HO = \left.\begin{matrix}N(C^{10}H^6O^2)H(C^{12}H^5)\\ H\end{matrix}\right\}O^2.\right]$$

*Combinations.* Dissolves in *water* rather more easily than pyrotartanil.

Combines with bases, and decomposes carbonates, but is precipitated from its own salts by acetic acid. The pyrotartanilates of the alkalis and earths dissolve very readily in water. The solution of the ammonia-salt does not precipitate the chlorides of barium and calcium, or lime or

baryta-water. With sulphate of *zinc*, it forms a cloud after some time only; with *sesquichloride of iron*, an orange-yellow precipitate; with sulphate of *copper* a bluish green; and with *mercuric* chloride a white precipitate.

The *Ammonia-salt* is obtained by boiling pyrotartanil with ammonia. It dries up to a radiated mass. Dissolves easily in cold water, but when boiled with water, it is decomposed and gives up its ammonia.

The *Potash-salt* resembles the ammonia-salt and dissolves very readily in water.

The *Soda-salt* dries up to a confusedly crystalline mass.

The *Baryta-salt*, when left for some time in the drying chamber, takes the form of crystalline grains.

The *Lime-salt* forms dull silky needles.

The *Lead-salt* forms a white precipitate which becomes glutinous by boiling, but when left to itself, acquires a granular and crystalline character, and then requires a rather high temperature to melt it. It dissolves in boiling water and in acetate of lead.

The *Silver-salt*, $C^{22}N^2H^{12}AgO^6$, is precipitated as a white pulverulent body, which dissolves in water and separates by evaporation in small round crystalline masses of the same composition. Contains 34·36 p. c. metallic silver.

Pyrotartanilic acid dissolves readily in *alcohol* and is precipitated from the solution by water in the crystalline state. Dissolves readily also in *ether*. (Arppe.)

## ¶. Pyrotartonitranilic Acid.

$$C^{22}N^2H^{12}O^{10} = C^{12}(C^{10}H^7O^2)AdXH^3,O^4 \text{ ?}$$

ARPPE. *Ann. Pharm.* 90, 145.

*Pyrotartronitranilic acid, Acide nitrophényl-protartramique.*

*Preparation.* By the action of alkaline carbonates on pyrotartonitranil. When that substance is introduced into a rather dilute and boiling solution of carbonate of soda, a yellow solution is formed which on cooling deposits crystals of β-nitraniline (p. 288), but retains pyrotartonitranilate of soda, from which the acid may be precipitated by nitric acid. It is thus obtained in yellow flakes, which may be purified by boiling with animal charcoal and recrystallisation.

From a saturated solution it is deposited in microscopic rhombic tables with angles of 60° and 120°. It melts at a little above 150°.

| *Dried over oil of vitriol.* | | | Arppe. |
|---|---|---|---|
| 22 C | 132 | 52·38 | 52·46 |
| 2 N | 28 | 11·11 | |
| 12 H | 12 | 4·76 | 4·89 |
| 10 O | 80 | 31·75 | |
| $C^{22}N^2H^{12}O^8$ | 252 | 100·00 | |

Pyrotartonitranilic acid is converted by boiling with alkaline carbonates into β-nitraniline.

It dissolves very sparingly in *water*.

It is a very feeble acid, not capable of decomposing carbonates. Some of its salts are very unstable, others uncrystallisable.

The ammonia-salt dries up to a syrup.

The *Potash-salt* scarcely exists in the solid state, for the solution of the acid in potash is easily decomposed and acquires a deep yellow colour.

*Silver-salt.* $C^{22}N^2H^{11}AgO^{10}$. — Crystalline flakes containing 30·13 p.c. silver.

The acid dissolves easily in *alcohol* and *ether*. (Arppe.) ¶.

## Amaniline.

$$C^{22}NH^{17} = C^{12}(C^{10}H^{11})NH^4,H^2.$$

A. W. Hofmann. *Ann. Pharm.* 74, 153; *Chem. Soc. Qu. J.* 3, 297.

*Mylanilin, Amylaniline, Amylophenylamine.—Formation* (*p.* 254).

*Preparation.* 1. A mixture of aniline and bromide of amyl is set aside at the ordinary temperature for several days; the mother-liquor, consisting of amaniline and bromide of amyl, decanted from the resulting crystals of hydrobromate of aniline; and the bromide of amyl distilled off:

$$2C^{12}NH^7 + C^{10}H^{11}Br = C^{12}NH^7,HBr + C^{22}NH^{17}.$$

2. A mixture containing a larger quantity of bromide of amyl is heated in the water-bath; the excess of bromide of amyl removed by distillation; and the remaining hydrobromate of amaniline decomposed by potash, whereby the amaniline is separated in the form of an oil, which may be purified by solution in ether, agitation with water, and evaporation of the ether.

*Properties.* Colourless oil, which boils steadily at 258° (therefore only 3·18° higher than ethaniline), has an agreeable odour like that of roses at ordinary temperatures, but an offensive odour of fusel-oil when heated.

| | | | Hofmann. |
|---|---|---|---|
| 22 C | 132 | 80·98 | 80·64 |
| N | 14 | 8·59 | |
| 17 H | 17 | 10·43 | 10·30 |
| $C^{22}NH^{17}$ | 163 | 100·00 | |

$(C^{12}H^5)(C^{10}H^{11})H,N$. (Hofmann.)

Heated with bromide of ethyl to 100°, it is converted into hydrobromate of ethamaniline, and with bromide of amyl into biamaniline:

$$C^{22}NH^{17} + C^4H^5Br = C^{26}NH^{21},HBr;$$

and:

$$C^{22}NH^{17} + C^{10}H^{11}Br = C^{32}NH^{27},HBr.$$

Its compounds with hydrobromic, hydrochloric and oxalic acids, form beautiful crystals, which have a fatty lustre, dissolve sparingly in water, and when heated with water, rise to the surface in the form of an oil which solidifies on cooling. — The chloroplatinate is precipitated in the form of an unctuous mass, which crystallises only after a considerable time, and when a portion of it has suffered decomposition. (Hofmann.)

## Methamaniline.

$$C^{24}NH^{19} = C^{12}(C^{10}H^{11})(C^2H^3)NH^3,H^2.$$

*Formemylaniline, Methylamylaniline, Methylamylophenylamine* = $C^{12}H^5,C^{10}H^{11},C^2H^3,N$, according to Hofmann.

Produced in the distillation of metethamaniline.

Oil having an agreeable odour.

The chloroplatinate is a crystalline precipitate which contains 15·81 p. c. platinum, and is therefore $C^{24}NH^{19},HCl + PtCl^2$. (Hofmann, *Ann. Pharm.* 79, 15.)

## Ethamaniline.

$$C^{26}NH^{21} = C^{12}(C^{10}H^{11})(C^4H^5)NH^3,H^2.$$

A. W. Hofmann. (1850.) *Ann. Pharm.* 74, 156, *Chem. Soc. Qu. J.* 3, 299.

*Vinemylanilin, Ethylamylaniline, Ethylamylophenylamine.*

*Preparation.* — A mixture of amaniline and excess of bromide of ethyl (*vid. sup.*), or of ethaniline and excess of bromide of amyl (p. 306), or of iodide of amyl, which acts most quickly, is heated in the water-bath for two days, and the alkaloid separated from the crystallised hydrobromate of ethamaniline in the ordinary way.

*Properties.* — Colourless oil, boiling at 262°, therefore only 4° higher than amaniline.

The *Hydrobromate* and *Hydrochlorate of Ethamaniline* crystallise. The former is resolved by distillation into ethaniline and bromide of amyl:

$$C^{26}NH^{21},HBr = C^{16}NH^{11} + C^{10}H^{11}Br.$$

The *Chloroplatinate* is precipitated in the form of an orange yellow viscid liquid, which solidifies in crystals fusible at 100°. (Hofmann.)

| | | | Hofmann. |
|---|---|---|---|
| 26 C | 156·0 | 39·27 | 39·00 |
| N | 14·0 | 3·52 | |
| 22 H | 22·0 | 5·54 | 5·70 |
| Pt | 99·0 | 24·93 | 24·64 |
| 3 Cl | 106·2 | 26·74 | |
| $C^{26}NH^{21},HCl + PtCl^2$ | 397·2 | 100·00 | |

## Biamaniline.

$$C^{32}NH^{2}I = C^{12}(C^{10}H^{11})^2NH^3,H^2.$$

A. W. Hofmann. (1850.) *Ann. Pharm.* 74, 155; *Chem. Soc. Qu. J.* 3, 298.

*Bimylaniline, Diamylaniline, Diamylophenylamine.*

Amaniline heated for two days in the water-bath with excess of bromide of amyl, yields crystals of hydrobromate of biamaniline (*vid. sup.*) from which the base may be separated in the usual way.

Oil, boiling between 275° and 280°, and having the odour of amaniline.

Its salts are nearly insoluble in water, so that when the base is heated with dilute hydrochloric or sulphuric acid, the resulting salt rises to the surface in the form of an oil, which on cooling solidifies in a crystalline mass having a fatty lustre. — The *platinum-salt* is precipitated, on mixing the hydrochlorate with bichloride of platinum, in the form of a yellow oil which quickly solidifies in a brick-red crystalline mass; alcoholic solutions immediately yield crystals.

| | | | Hofmann. |
|---|---|---|---|
| 32 C | 192·0 | 43·72 | 43·60 |
| N | 14·0 | 3·19 | |
| 28 H | 28·0 | 6·37 | 6·50 |
| Pt | 99·0 | 22·54 | 22·38 |
| 3 Cl | 106·2 | 24·18 | |
| $C^{32}NH^{27},HCl + PtCl^2$ | 439·2 | 100·00 | |

$= C^{12}H^5(C^{10}H^{11})^2,N$. (Hofmann.)

## Metethamaniline.

$$C^{28}NH^{23} = C^{12}(C^{10}H^{11})(C^4H^5)(C^2H^3)NH^2,H^2.$$

A. W. Hofmann. *Ann. Pharm.* 79, 13; *Chem. Soc. Qu. J.* 4, 319.

*Formevinemylanilin.* (Gm.) — Supposing it to contain 1 H more, it will be *Methylethylamylophenylammonium* = $C^{12}H^5,C^{10}H^{11},C^4H^5,C^2H^3,N$. (Hofmann.)

Known only in combination with water and with hydriodic acid.

The clear mixture of ethamaniline $C^{12}(C^{10}H^{11})(C^4H^5)NH^5$, with iodide of methyl $C^2H^3I$, heated in a sealed tube in the water-bath, separates into two layers, the lower of which continually increases, and on cooling, solidifies as a mixture of hydriodate of metethamaniline and hydriodate of ethamaniline. By dissolving the mass in water; setting the solution aside, and separating it from the undecomposed iodide of methyl; digesting the solution with oxide of silver; filtering from the iodide of silver and excess of oxide of silver, and the separated ethamaniline (which is insoluble in water), — a solution of metethamaniline is obtained; and this, when evaporated, leaves a hydrate, which is resolved by distillation into water, olefiant gas and methamaniline:

$$C^{28}NH^{23},2HO = 2HO + C^4H^4 + C^{24}NH^{19}.$$

The *chloroplatinate* is a pale yellow, non-crystalline precipitate which contains 24·11 p. c. platinum, and is therefore $C^{28}NH^{23},HCl + PtCl^2$. (Hofmann.)

## Ethaniline-urea.

$$C^{18}N^2H^{12}O^2 = C^{12}(C^4H^5)CyAdH^3,H^2O^2. ?$$

Wurtz. (1851.) *Compt. rend.* 32, 417.

*Phenyethyl-urea* = $C^2N^2(C^{12}H^5)(C^4H^5)H^2O^2$.

The solution of aniline in cyanuric ether, (ix 459), the formation of which is attended with great rise of temperature, solidifies on cooling in a crystalline mass:

$$C^{12}NH^7 + C^6NH^5O^2 = C^{18}N^2H^{12}O^2.$$

The compound is slowly decomposed by potash into aniline, ethylamine and carbonic acid. (Wurtz.)

$$C^{18}N^2H^{12}O^2 + 2KO + 2HO = C^{12}NH^7 + C^4NH^7 + 2(KO,CO^2).$$

## ¶. Valeranilide.

$$C^{22}NH^{15}O^2 = C^{12}(C^{10}H^9O^2)NH^4,H^2. ?$$

Chiozza. (1852.) *N. Ann. Chim. Phys.* 39, 201.

*Phenyl-valeramide.*

Obtained by the action of anhydrous valerianic acid upon aniline. The mixture of the two substances becomes very hot, and after a while solidifies in a mass of beautiful crystals of valeranilide, which may be purified by recrystallisation from boiling alcohol.

Fine needles or elongated laminæ, having a strong lustre, and often of considerable size. By spontaneous evaporation of its solution in a mixture of alcohol and ether, it is obtained in lengthened prisms formed by the aggregation of a number of smaller crystals. Sometimes, when it separates from a solution in boiling dilute alcohol, it takes the form of oily drops, which remain fluid for several hours, even after the liquid has completely cooled, but, on the slightest agitation, solidify in a mass of slender needles. The compound melts at 115°, and distils for the most part unaltered at a temperature above 220°. It is but very slowly attacked by caustic potash, even at a boiling heat; and it is only by fusion with hydrate of potash, that an appreciable quantity of aniline can be separated from it.

| | | |
|---|---|---|
| 22 C | 132 | 74·58 |
| N | 14 | 7·91 |
| 15 H | 15 | 8·48 |
| 2 O | 16 | 9·03 |
| $C^{22}NH^{15}O^2$ | 177 | 100·00 |

$= N(C^{12}H^5)(C^{10}H^9O^2)H$ = nitride of phenyl, valeral and hydrogen.

Dissolves sparingly in boiling *water*, readily in *alcohol* and *ether*.

## ¶. Biphenaniline.

$$C^{36}NH^{15} = C^{12}(C^{12}H^5)^2NH^3,H^2.$$

A. GÖSSMANN. *Ann. Pharm.* 100, 57.

*Triphenylamine.*

*Formation* and *Preparation*. By the distillation of sulphite of cinnamyl and ammonium ($C^{18}H^7O, NH^4O, 2SO^2$), with hydrate of lime.

$$[2C^{18}H^7O + 2NH^4O = C^{36}NH^{15} + 4HO + NH^3.]$$

The distillate, which consists of a dark yellow oily liquid and a watery ammoniacal liquid containing the biphenaniline, is boiled with carbonate of soda or dilute potash-ley, till all the ammonia and volatile hydrocarbon, &c., are expelled; the fixed alkali removed by repeated washing, with diminishing quantities of hot water; and, after the water has been separated as completely as possible by decantation, the oily base is distilled in a slow stream of hydrogen, the temperature being kept low at first to evaporate the water, and the base afterwards distilled off between 140° and 150; this temperature should be kept up as long as possible, since the base decomposes at higher temperatures.

*Properties.* Colourless oily liquid, which, on exposure to the air, becomes yellow at first, and afterwards red. Boils between 140° and 150°.

*Combinations.* Biphenaniline dissolves sparingly in water, forming an alkaline solution.

The *salts* are very unstable, all of them, excepting the platinum-salts, decomposing spontaneously on exposure to the air, either in aqueous or in alcoholic solution.

*Hydrochlorate of Biphenaniline.* — When strong hydrochloric acid is added to pure biphenaniline, the base remains oily at first, but, on addition of alcohol of 95 per cent. suddenly solidifies and forms a crystalline salt, which may be purified by washing with absolute alcohol. Shining laminæ, having a slight tinge of red, Tolerably stable when protected from air and moisture. Dissolves easily in water and common alcohol, less easily in absolute alcohol and anhydrous ether.

*Chloroplatinate of Biphenaniline.* — Separates on mixing the alcoholic solution of hydrochlorate of biphenaniline with a moderately strong and neutral alcoholic solution of bichloride of platinum, as a dark yellow, bulky, flocculent precipitate, which may be washed with alcohol of 95 p. c. The salt is permanent in the air. It dissolves in alcohol of 75 to 80 p. c.: and separates when the solution is evaporated over oil of vitriol, in brown crystals belonging to the regular system and having a glassy lustre.

| | | | Gössmann (*mean*). |
|---|---|---|---|
| 36 C | 216·0 | 47·88 | 47·59 |
| N | 14·0 | 3·10 | |
| 16 H | 16·0 | 3·55 | 3·52 |
| Pt | 99·0 | 21·86 | 23·18 |
| 3 Cl | 106·2 | 23·61 | |
| $C^{36}NH^{15},HCl + PtCl^2$ | 451·2 | 100·00 | |

*Biphenaniline with Bichloride of Platinum.* — Separates as a bulky precipitate, when an alcoholic solution of the base is mixed with an alcoholic and perfectly neutral solution of bichloride of platinum. Has a somewhat brighter colour than the chloroplatinate, and dissolves in the same manner in water and in hydrated alcohol. Absorbs moisture from the air when recently precipitated, but remains unaltered after drying.

| | | | Gössmann (*mean*). |
|---|---|---|---|
| 36 C | 216·0 | 52·08 | 52·22 |
| N | 14·0 | 3·38 | |
| 15 H | 15·0 | 3·62 | 3·88 |
| Pt | 99·0 | 23·80 | 23·39 |
| 2 Cl | 70·8 | 17·12 | |
| $C^{36}NH^{15},PtCl^2$ | 414·8 | 100·00 | |

May be regarded as *bichloride of platinotriphenylammonium* = $C^{36}NH^{15}Pt,Cl^2$, or as *chloride chloroplatino-triphenylammonium* = $C^{36}N\left\{\begin{matrix}H^{15}\\PtCl\end{matrix}\right\},Cl$.

Biphenaniline combines also with *mercuric chloride* and *nitrate of silver.* The mercury-compound crystallises in laminæ, but decomposes

on recrystallisation. The silver-compound is but slightly crystalline and soon changes colour from yellowish white to brown.

*Oxalate of Biphenaniline.* — Crystallises in needles which absorb moisture from the air.

Biphenaniline dissolves readily in *alcohol* and *ether*. (Gössman.)

## ¶. Biphenethaniline.

$$C^{40}NH^{19} = C^{12}(C^4H^5)(C^{12}H^5)^2NH^2,H^2.$$

GÖSSMANN. *Ann. Pharm.* 100, 65.

Supposing it to contain 1 H more, it may be regarded as *Ethytriphenylammonium* = $(C^4H^5)(C^{12}H^5)^3N$. It is not known in the separate state.

Obtained as an hydriodate by the action of an excess of iodide of ethyl at 100° on biphenaniline; the action takes place also at common temperatures, but more slowly.

The *hydrate* is obtained by treating the alcoholic solution of the hydriodate with oxide of silver, filtering, removing a small portion of dissolved oxide of oilver by hydrochloric acid, and mixing the alcoholic solution with a small quantity of water. The base then separates in the form of an oily liquid, which dissolves sparingly in water, easily in alcohol; does not change colour in solution at ordinary temperatures; but is decomposed when its aqueous solution is boiled, depositing oily drops. It has a strong, but agreeable bitter taste, no smell, and a strong alkaline reaction. Its solution, as well as that of the hydrochlorate, exhibits distinct fluorescence. It dissolves oxide of silver, and combines also with acids forming salts which seem to be all liquid.

*Chloroplatinate.* — Precipitated in yellow microscopic crystals, when neutral bichloride of platinum is added to a moderately concentrated solution of the hydrochlorate. Dissolves in water, and separates in the crystalline form by spontaneous evaporation. When boiled with a quantity of water not sufficient to dissolve it, it melts into a resinous mass, which exhibits a distinct crystalline fracture. The crystals become darker and lose their lustre between 90° and 100°, but do not undergo any further alteration at 120°.

| *Dried at* 120°. | | | Gössmann (*mean*). |
|---|---|---|---|
| 40 C | 240·0 | 50·08 | 49·96 |
| N | 14·0 | 2·92 | 2·91 |
| 20 H | 20·0 | 4·17 | 4·19 |
| Pt | 99·0 | 20·60 | 20·78 |
| 3 Cl | 106·2 | 22·23 | 21·80 |
| $C^{40}NH^{19},HCl + PtCl^2$ | 479·2 | 100·00 | |

= $C^{40}NH^{20}Cl,PtCl^2$. (Gössmann.) ¶.

*Conjugated Compounds of 2 At.* $C^{12}NH^5$ *or a similar Nucleus.*

The nucleus contains 24 C and 12 H or other substances.

## Azobenzene.

$C^{24}N^2H^{10}$.

Mitscherlich (1834). *Pogg.* 32, 224.
Zinin. *J. pr. Chem.* 36, 93.

*Azobenzid, Azobenzol, Stickstoffbenzid, Azodifune.*

*Preparation.* 1. In distilling a mixture of the alcoholic solutions of nitrobenzene and potash, a red liquid passes over towards the end, which, on cooling solidifies in a crystalline mass. This mass is pressed between paper and recrystallised from ether. (Mitscherlich.) — 2. The mixture of azobenzene and aniline obtained by the dry distillation of azoxibenzene is freed from the greater part of the more volatile aniline by fractional distillation, pressing the residue between paper, and crystallising it from alcohol. The small quantity of azobenzene which passes over with the aniline, separates as a heavy oil when the aniline is dissolved in hot dilute sulphuric acid. (Zinin.) — ¶ 3. When nitrobenzene is treated with iron turnings and acetic acid, as in Béchamp's process for the preparation of aniline, but with the proportion of iron considerably greater than that which Béchamp recommends (viz. 3 pts. iron to 2 pts. nitrobenzene and 2 pts. acetic acid, p. 247), the first portion of the distillate consists principally of aniline mixed with a small quantity of nitrobenzene, but the last third is a dark red liquid which solidifies in the neck of the retort and in the condensing tube as a beautifully crystallised mass of azobenzene. The best product is obtained by using 3 pts. of iron to 1 pt. of nitrobenzene and 1 pt. of acetic acid. The red crystalline mass is washed with hydrochloric acid to remove adhering alcohol, then with water; dissolved in boiling alcohol; and the red crystalline laminæ which separate on cooling, again dissolved in alcohol and recrystallised. (A. Noble, *Chem. Soc. Qu. J.* 8, 292.) — 4. Benzidine treated with nitrous acid vapours is converted into azobenzene. (Noble). ¶.

*Properties.* Large red crystals which melt at 65°, boil at 193°, and distil without decomposition. (Mitscherlich.)

| | | | Mitscherlich. | Noble. *a.* | *b.* |
|---|---|---|---|---|---|
| 24 C | 144 | 79·12 | 79·16 | 79·19 | 79·02 |
| 2 N | 28 | 15·39 | 14·95 | | |
| 10 H | 10 | 5·49 | 5·45 | 5·69 | 5·78 |
| $C^{24}N^2H^{10}$ | 182 | 100·00 | 99·56 | | |

*a.* prepared by (3); *b.* by (4).

*Decompositions.* 1. Its vapour passed through a red-hot tube decomposes without explosion. (Mitscherlich.) — 2. Its orange-yellow solution in cold fuming nitric acid, becomes heated, soon assumes a blood-red colour, then gives off red vapours, and solidifies in a pulpy mass of yellowish-red needles (sparingly soluble in hot nitric acid). This mass, after being separated from the mother-liquor and dissolved in boiling alcohol, separates into small rhombic tables (binitrazobenzene, according to Laurent & Gerhardt) having an aurora-red colour and almost metallic lustre, which separate on cooling and dissolve but slowly in alcohol and ether,— and dull straw-coloured slender needles (nitrazobenzene, according to Laurent & Gerhardt) which remain dissolved in the alcohol. (Zinin.) — 3. Oil of vitriol boiled with azobenzene gives off sulphurous acid and deposits charcoal. (Mitscherlich.) — 4. The aurora-red solution in alcoholic ammonia, on being saturated with sulphuretted hydrogen, gradually assumes a light yellow colour, and as it cools, deposits a considerable quantity of large white laminæ. These crystals dissolve when heated with the liquid, and the black-brown solution when boiled, deposits a large quantity of sulphur-powder, assumes a light red colour, and, after being decanted from the sulphur, yields on cooling, yellowish-white needles and laminæ of benzidine, whilst an aurora-red mother-liquor remains. (Zinin.) — Azobenzene may be distilled over potash or lime without decomposition (Mitscherlich); its vapour is not decomposed by potash-lime at 250°. (Laurent & Gerhardt.)

*Combinations.* Azobenzene dissolves very sparingly in boiling *water*, the solution becoming turbid as it cools.

From its solution in strong *sulphuric* or *nitric acid*, it is precipitated by water.

It dissolves very sparingly in strong *hydrochloric acid*, and in aqueous *ammonia* or *potash*.

It dissolves abundantly in *alcohol* and *ether*, and crystallises as the solution evaporates. (Mitscherlich.)

## Benzidine.

$$C^{24}N^2H^{12} = C^{24}N^2H^{10},H^2.$$

ZININ. (1845.) *J. pr. Chem.* 36, 93.

*Funidin.*

*Preparation.* Sulphuretted hydrogen is passed to saturation through the aurora-red solution of azobenzene in alcohol saturated with ammoniacal gas; the liquid, which has become light yellow, is boiled for some time, whereupon the white crystalline laminæ which have formed, dissolve, with black-brown colour; and the liquid, which ultimately acquires a light reddish-yellow colour, is decanted while hot from the copious precipitate of sulphur-powder, and then cooled, whereupon it yields yellowish-white laminæ of impure benzidine, which acquire a deeper yellow colour when kept in a close vessel, and when examined by a lens, appear to be mixed with aurora-red needles and yellow granules. It is therefore dissolved in

boiling alcohol; moderately dilute sulphuric acid added, as long as any white powder of sulphate of benzidine is precipitated; and this precipitate washed with cold alcohol, till the liquid runs through colourless; then dissolved in boiling dilute ammonia; and the scales of pure benzidine which are deposited as the filtrate cools, are dried in vacuo over oil of vitriol. Benzidine may also be obtained from azoxibenzene and hydrosulphate of ammonia. (Laurent & Gerhardt.)

*Properties.* Snow-white scales having a silvery lustre. Becomes somewhat duller at 100°; melts at 108°, forming a nearly colourless liquid, which at 108° or 112°* solidifies into a brownish-white crystalline mass. Inodorous; its solutions have a biting peppery and bitter alkaline taste; permanent in the air.

| *Dried in a stream of air at* 100°. | | | Zinin. |
|---|---|---|---|
| 24 C | 144 | 78·26 | 78·02 |
| 2 N | 28 | 15·22 | 14·79 |
| 12 H | 12 | 6·52 | 6·66 |
| $C^{24}N^2H^{12}$ | 184 | 100·00 | 99·47 |

*Decompositions.* 1. Benzidine heated above its melting point turns brown, begins to boil, and sublimes partly undecomposed, partly in resinous decomposition-products, and leaves a residue of charcoal. — 2. The aqueous or alcoholic solution of benzidine or its salts, assumes a red-brown colour when chlorine gas is passed through it, often however after previously exhibiting an indigo-colour; becomes turbid; and deposits a large quantity of a crystalline powder nearly insoluble in water, more soluble in alcohol. — 3. Its brown-red solution in strong nitric acid assumes a lighter colour and gives off nitrous fumes when heated, and afterwards yields with water red-brown flakes, sparingly soluble in alcohol, together with a supernatant yellow liquid from which ammonia still throws down a considerable quantity of brown flakes, imparting at the same time a blood-red colour to the liquid.—4. Nitrous acid converts it into azobenzene. (Noble.)

*Combinations.* Benzidine dissolves very sparingly in cold *water,* but so abundantly in hot water, that a solution saturated while hot solidifies in a solid pulp on cooling.

It forms with acids, white, easily crystallising *salts,* which are precipitated by caustic ammonia and potash or their carbonates.—Assuming, as is here done, with Laurent & Gerhardt (*Compt. chim.* 1849, 166) that benzidine $= C^{24}N^2H^{12}$, and not, with Zinin, that it is $C^{12}NH^6$, all its salts must be regarded as bi-acid.

*Phosphate of Benzidine.* — Ordinary phosphoric acid added to a dilute aqueous solution of benzidine, throws down small nacreous scales, and from the concentrated solution a slightly crystalline powder. The salt is as little soluble in water as the sulphate.

*Sulphate of Benzidine.—a. Bi-acid.*— Precipitated by sulphuric acid from a very dilute aqueous solution of benzidine, in the form of a dull

* One or other of these numbers must be a misprint in Zinin's paper.

white powder, and from a still more dilute solution in nacreous microscopic scales. Nearly insoluble in water and in alcohol.

| *Dried at* 100°. | | | | Zinin. |
|---|---|---|---|---|
| 24 C | 144 | .... | 51·06 | 50·64 |
| 2 N | 28 | .... | 9·93 | |
| 14 H | 14 | .... | 4·97 | |
| 2 O | 16 | .... | 5·67 | 5·10 |
| 2 $SO^3$ | 80 | .... | 28·37 | 28·47 |
| $C^{24}N^2H^{12},2HO,2SO^3$ | 282 | .... | 100·00 | |

*b. Hyperacid.* — The yellowish solution of benzidine in cold or slightly heated oil of vitriol, remains liquid even in the cold, but on a slight addition of water, crystallises at ordinary temperatures in a radiated mass, and on a larger addition of water, solidifies in a pulp consisting of the pulverulent salt *a*.

*Hydrochlorate of Benzidine.* — Crystallises from water or alcohol in white, nacreous, rhombic laminæ, which are not altered by exposure to the air, or by a temperature of 100°; but, if exposed to the air in contact with ether or acids, acquire a dirty green colour, and lose their crystalline form.

| | | | | Zinin. |
|---|---|---|---|---|
| 24 C | 144·0 | .... | 56·08 | 56·12 |
| 2 N | 28·0 | .... | 10·90 | |
| 14 H | 14·0 | .... | 5·45 | 5·64 |
| 2 Cl | 70·8 | .... | 27·57 | 27·28 |
| $C^{24}N^2H^{12},2HCl$ | 256·8 | .... | 100·00 | |

*Nitrate of Benzidine.* — The solution of benzidine in warm dilute nitric acid, yields on cooling thin right-angled laminæ, permanent in the air.

Benzidine forms with protochloride of mercury a double salt having the form of white shining laminæ easily soluble in water and alcohol.

*Chloroplatinate of Benzidine.* — The yellow crystalline precipitate which an aqueous or alcoholic solution of hydrochlorate of benzidine forms with bichloride of platinum. This precipitate when heated with water is decomposed at the boiling heat, but not below; it is also decomposed by alcohol, especially when hot, and still more quickly by ether, and converted into a dark violet powder. It dissolves sparingly in water, and scarcely at all in alcohol or ether.

| *Dried in vacuo over oil of vitriol.* | | | | Zinin. | Noble. |
|---|---|---|---|---|---|
| 24 C | 144·0 | .... | 24·15 | | |
| 2 N | 28·0 | .... | 4·69 | | |
| 14 H | 14·0 | .... | 2·35 | | |
| 2 Pt | 198·0 | .... | 33·19 | 33·03 | 33·09 |
| 6 Cl | 212·4 | .... | 35·62 | | |
| $C^{22}N^2H^{12},2HCl + 2PtCl^2$ | 596·4 | .... | 100·00 | | |

*Acetate of Benzidine.*—White, shining, thin, elongated laminæ, easily soluble in water and alcohol.

*Oxalate of Benzidine.* — Delicate silky needles united in stellate groups, permanent in the air, not changing at 100°, dissolving with some difficulty in water and alcohol.

| *Crystals.* | | | Zinin. |
|---|---|---|---|
| 28 C | 168 | 61·31 | 61·46 |
| 2 N | 28 | 10·22 | |
| 14 H | 14 | 5·11 | 5·39 |
| 8 O | 64 | 23·36 | |
| $C^{24}N^2H^{12},C^4H^2O^8$ | 274 | 100·00 | |

*Tartrate of Benzidine.* — White shining laminæ resembling benzidine, but more easily soluble in water.

Benzidine dissolves readily in *alcohol,* and still more readily in *ether.* (Zinin.)

## Azoxybenzene.

$$C^{24}N^2H^{10}O^2 = C^{24}N^2H^{10},O^2.$$

Zinin. (1845.) *J. pr. Chem.* 36, 98.
Laurent & Gerhardt. *Compt. chim.* 1849, 417; also *Ann. Pharm.* 75, 70.

*Azoxybenzid, Azoxydifune.*

*Preparation.* 1 pt. of pulverized hydrate of potash is added to a solution of 1 pt. of nitrobenzene in a tenfold volume of alcohol, the liquid boiled as soon as the heat spontaneously developed has subsided; the brown needles of azoxybenzene which already separate on cooling, collected; the remaining liquid distilled till it separates into two layers, (p 202 ), and the upper brown oily layer decanted and washed with water; it then solidifies after a few hours in a mass of needles of impure azoxybenzene. These crystals, together with the needles previously obtained, are strongly pressed between paper, and purified by several crystallisations from alcohol and ether. The purification may be accelerated by passing chlorine through the brown solution in hot alcohol till it turns yellow. (Zinin.)

*Properties.* Yellow, shining, four-sided needles, and (by spontaneous evaporation of the ethereal solution) prisms an inch long, as hard as sugar, and easily friable. Melts at 36° into a yellow, strongly refracting liquid, which, at a temperature immediately below 36°, solidifies in a radiated mass.

| *Crystals dried over oil of vitriol.* | | | Zinin. |
|---|---|---|---|
| 24 C | 144 | 72·72 | 72·65 |
| 2 N | 28 | 14·15 | 13·99 |
| 10 H | 10 | 5·05 | 5·28 |
| 2 O | 16 | 8·08 | 8·08 |
| $C^{24}N^2H^{10}O^2$ | 198 | 100·00 | 100·00 |

*Decompositions.* 1. Azoxybenzene heated to the *boiling point* assumes a greenish-brown colour, leaves a tumefied carbonaceous mass, and gives off yellow vapours, which condense into a liquid mixture of impure aniline and azoxybenzene. The first portions of the distillate are comparatively rich in aniline, and remain liquid on cooling, while the middle portions are buttery, and the last portions, which contain a gradually increasing proportion of azoxybenzene, solidify on cooling. — 2. By *bromine* it is converted into bromazoxybenzene. (Laurent & Gerhardt.) — *Chlorine* does not exert any decomposing action on azoxybenzene, either in the fused state or dissolved in alcohol. — 3. Ordinary nitric acid acts but slightly on azoxybenzene, even at the boiling heat; but the yellowish-red solution in cold fuming nitric acid becomes spontaneously heated, gives off red vapours, and then solidifies on cooling in a mass of soft yellow needles (consisting, according to Laurent & Gerhardt, of nitrazoxybenzene $C^{24}N^2XH^9O^2$). (Zinin.) — 4. Its yellowish-red solution in slightly heated oil of vitriol, deposits, on addition of water, a small quantity of greenish oil, which soon solidifies as azoxybenzene mixed with a greenish resin, whilst the water appears to retain a conjugated sulphuric acid. (Zinin.) — 5. Hydrosulphate of ammonia converts it into benzidine. (Laurent & Gerhardt, *Compt. Chem.* 1849, 166.) [Probably thus: $C^{24}N^2H^{10}O^2 + 4HS = C^{24}N^2H^{12} + 2HO + 4S$.]

*Combinations.* It does not dissolve in water, aqueous sulphuric acid, ammonia or potash.

It dissolves readily in *alcohol* and still more readily in *ether*. From its solution in alcoholic hydrochloric acid, it is precipitated in its original state by alcoholic ammonia or potash. (Zinin.)

## Bromazoxybenzene.

$$C^{24}N^2BrH^9O^2 = C^{24}N^2BrH^9,O^2.$$

LAURENT & GERHARDT. *Compt. chim.* 1849, 417; also *Ann. Pharm.* 75, 72.

*Gebromtes Azoxybenzid, Azoxybenzide bromé, Bromazoxydifune.*

Azoxybenzene is converted by bromine into a yellowish, easily fusible substance which solidifies in crystalline nodules on cooling, and dissolves very sparingly in alcohol. (Laurent & Gerhardt.)

| | | | Laurent & Gerhardt. |
|---|---|---|---|
| 24 C | 144 | 51·98 | 46·7 |
| 2 N | 28 | 10·11 | |
| Br | 80 | 28·88 | 31·9 |
| 9 H | 9 | 3·25 | 2·7 |
| 2 O | 16 | 5·78 | |
| $C^{24}N^2BrH^9O^2$ | 277 | 100·00 | |

The substance analysed was doubtless contaminated with a higher bromine-compound. (Laurent & Gerhardt.)

## Nitrazobenzene.

$C^{24}N^3H^9O^4 = C^{24}N^2XH^9$.

Zinin. (1845.) *J. pr. Chem.* 36, 103.
Laurent & Gerhardt. *Compt. chim.* 1849, 417; also *Ann. Pharm.* 75, 73.

*Nitrazobenzid, Nitrazodifune.*

*Preparation.* 1. The crystalline magma produced by the action of fuming nitric acid on azobenzene is drained in a filter plugged with asbestus, and afterwards on a brick to free it from the mother-liquor; the residue dissolved in strong boiling alcohol; and the yellow nitrazobenzene, which is more readily soluble in alcohol and ether, separated by repeated crystallisation from the binitrazobenzene which crystallises much more easily. (Zinin.) — Azobenzene is gently heated with fuming nitric acid; the liquid left to cool after the action is finished; the mother-liquor decanted from the yellowish-red mass of needle-shaped crystals thus produced; the crystals washed with ordinary nitric acid, then with a little water, and boiled with alcohol; the oil decanted [from the binitrazobenzene ?]; and the needles which separate therefrom, washed with a small quantity of alcohol and ether to remove an oily product. (Laurent & Gerhardt.)

*Properties.* — Slender needles of a dull straw-yellow colour. Pale orange-yellow, somewhat laminated needles, fusing more readily than binitrazobenzene, and crystallising as the liquid cools. (Laurent & Gerhardt.)

| | | | Laurent & Gerhardt. |
|---|---|---|---|
| 24 C | 144 | 63·44 | 62·5 |
| 3 N | 42 | 18·50 | 18·1 |
| 9 H | 9 | 3·96 | 3·9 |
| 4 O | 32 | 14·10 | 15·5 |
| $C^{24}N^3H^9O^4$ | 227 | 100·00 | 100·0 |

It dissolves in alcohol less readily than azobenzene, but more readily than binitrazobenzene. (Laurent & Gerhardt.)

## Nitrazoxybenzene.

$C^{24}N^3H^9O^6 = C^{24}N^2XH^9,O^2$.

Zinin. (1845.) *J. pr. Chem.* 36, 99.
Laurent & Gerhardt. *Compt. chim.* 1849; also *Ann. Pharm.* 75, 71.

*Nitrazoxybenzid, Nitrazoxydifune.*

*Preparation.* The needles formed after the cooling of a solution of azobenzene in fuming nitric acid (p. 338), are drained on asbestus, dried on a brick, and crystallised from hot alcohol. The alcoholic mother-liquor yields by evaporation, yet another body, in four-sided prisms, which dissolve very easily in alcohol and ether, and without decomposition in fuming nitric acid at the boiling heat. (Zinin.) — Laurent and Gerhardt heat the nitric acid solution to the boiling point.

*Properties.* Dull yellow needles united in tufts. (Laurent & Gerhardt.)

| | | | Laurent & Gerhardt. |
|---|---|---|---|
| 24 C | 144 | 59·26 | 58·8 |
| 3 N | 42 | 17·29 | 16·5 |
| 9 H | 9 | 3·70 | 3·6 |
| 6 O | 48 | 19·75 | 21·1 |
| $C^{24}N^3H^9O^6$ | 243 | 100·00 | 100·0 |

The red-brown solution of the yellow needles in alcoholic potash deposits, when evaporated with water, an aurora-red, crystalline powder, which decomposes when heated, and is nearly insoluble in alcohol and ether; it contains 70·1 p. c. C, 17·5 N, 4·5 H, and 7·9 O, and is therefore perhaps $C^{48}N^5H^{19}O^4$ or $C^{24}N^3H^9O^2$. (Laurent & Gerhardt.)

The needles dissolve in fuming *nitric acid* at the boiling heat, and crystallise undecomposed on cooling. (Zinin.)

They dissolve sparingly in *alcohol* (and in *ether*, according to Laurent & Gerhardt), and crystallise on cooling. (Zinin.)

## Binitrazobenzene.

$C^{24}N^4H^8O^8 = C^{24}N^2X^2O^8$.

ZININ. (1845.) *J. pr. Chem.* 36, 103.
LAURENT & GERHARDT. *Compt. chim.* 1849, 417; also *Ann. Pharm.* 75, 74.

*Binitrazobenzid, Binitrazodifune.*

*Preparation.* 1. According to Zinin (p. 343). — 2. Azobenzene is boiled for some minutes with fuming nitric acid; the mother-liquor, when cold, decanted from the red needles; and these needles washed with ordinary nitric acid, then with water, then with ether, and crystallised from boiling alcohol. (Laurent & Gerhardt.)

*Properties.* Small rhombic tables, having an aurora-red colour and almost metallic lustre (Zinin); aurora-red needles, less fusible than nitrazobenzene, and forming a blood-red liquid which crystallises in needles. (Laurent & Gerhardt.)

| | | | | | Laurent & Gerhardt. |
|---|---|---|---|---|---|
| 24 C | 144 | .... | 52·94 | ........ | 52·4 |
| 4 N | 56 | .... | 20·59 | | |
| 8 H | 8 | .... | 2·94 | ........ | 2·9 |
| 8 O | 64 | .... | 23·53 | | |
| $C^{24}N^4H^8O^8$ | 272 | .... | 100·00 | | |

Boiled with hydrosulphate of ammonia and with alcohol, it is converted into diphenine. (Laurent & Gerhardt.)

$$C^{12}N^4H^8O^8 + 12HS = 2C^{12}N^6H^6 + 8HO + 12S.$$

It dissolves without decomposition in boiling *nitric acid*, and separates therefrom in finer crystals than from alcohol. (Laurent & Gerhardt.)

It is nearly insoluble in cold, and very sparingly soluble in boiling *alcohol* and *ether*. (Zinin.)

## Binitrodiphenamic Acid.

$$C^{24}N^4H^{12}O^{12} = C^{24}X^2Ad^2H^8,O^4.$$

LAURENT & GERHARDT. (1849.) *Compt. chim.* 1849; abstr. *Ann. Pharm.* 75, 68.

*Binitrodifunamsäure, Binitrodiphänaminsäure, Acide binitrodiphénamique.*

The black-brown mass of needle-shaped crystals obtained by gently heating binitrocarbolic acid with hydrosulphate of ammonia (p. 206), is boiled with excess of acetic acid, the liquid filtered hot to separate sulphur, and the acid left to crystallise from the filtrate.

Black-brown, thick, six-sided needles with four lateral edges of 131° 30′ and two of 97°; they yield a brown powder and give off their 4 atoms of water of crystallisation between 100° and 150°.

| *Crystals with 4 Aq.* | | | | | Laurent & Gerhardt. |
|---|---|---|---|---|---|
| 24 C | 144 | .... | 41·86 | ........ | 42·0 |
| 4 N | 56 | .... | 16·28 | ........ | 16·5 |
| 16 H | 16 | .... | 4·65 | ........ | 4·6 |
| 16 O | 128 | .... | 37·21 | ........ | 36·9 |
| $C^{24}N^4H^{12}O^{12} + 4Aq$ | 344 | .... | 100·00 | | 100·00 |

The crystals when heated, first give off their water, then melt, yielding a sublimate of a few laminæ and a small quantity of a brown oily distillate, and leave a large quantity of charcoal which takes fire at a somewhat higher temperature.

The deep red solution of the acid in aqueous *ammonia* gives off the ammonia when evaporated, and leaves the pure acid.

The brown-red solution of the acid in aqueous *potash* yields the potash-salt by spontaneous evaporation, in deep red crystalline nodules

which dissolve very readily in water and alcohol, and, when dried at 100°, contain 10·7 per cent. of potash, and are therefore $C^{24}N^4H^{11}KO^{12}$.

The ammoniacal solution of the acid forms with acetate of *baryta*, red-brown, sparingly soluble needles;—with *lime-salts*, after a while, small needles;—with acetate of *lead*, a yellowish red-brown precipitate; —with *cupric* acetate, a yellowish-green precipitate; and with nitrate of *silver*, a deep yellowish-brown precipitate, which, when warm solutions are used, crystallises in laminæ. (Laurent & Gerhardt.)

| *Silver-salt.* | | | | Laurent & Gerhardt. |
|---|---|---|---|---|
| 24 C | 144 | .... | 34·70 | 34·7 |
| 4 N | 56 | .... | 13·49 | |
| 11 H | 11 | .... | 2·66 | 2·6 |
| Ag | 108 | .... | 26·02 | 26·4 |
| 12 O | 96 | .... | 23·13 | |
| $C^{24}N^4H^{11}AgO^2$ | 415 | .... | 100·00 | |

## ¶. Nitrosulphobenzene.

$$C^{24}NH^9S^2O^8 = C^{24}XH^9(SO^2)^2.$$

H. Gericke. *Ann. Pharm.* 100, 208.

When sulphobenzene (p. 165) is heated with fuming nitric acid, and the resulting liquid mixed with water, a precipitate is formed consisting of nitrosulphobenzene and binitrosulphobenzene, the former of which may be extracted by hot alcohol, while the greater part of the latter remains undissolved; and the alcoholic solution, on cooling, deposits the nitrosulphobenzene in the form of a honey-yellow, unctuous, plastic mass, which gradually solidifies. From a solution in dilute alcohol, it separates by spontaneous evaporation in soft microscopic crystals having their faces lenticularly rounded. — The solution frequently also deposits crystals of sulphobenzene.

Nitrosulphobenzene melts between 90° and 95°, and is completely decomposed at 250°. Sulphide of ammonium converts it into amidosulphobenzene.

| | | | | Gericke. |
|---|---|---|---|---|
| 24 C | 144 | .... | 54·7 | 55·5 |
| N | 14 | .... | 5·3 | |
| 9 H | 9 | .... | 3·4 | 4·0 |
| 2 S | 32 | .... | 12·2 | 12·7 |
| 8 O | 64 | .... | 24·4 | |
| $C^{24}NH^9S^2O^8$ | 263 | .... | 100·0 | |

$= C^{12}XH^4SO^2,C^{12}H^5SO^2$. (Gericke.)

Insoluble in cold *water*, and dissolves but sparingly in hot water, whence it separates in oily drops on cooling. Dissolves in *nitric acid*, but not in sulphuric or hydrochloric acid. Caustic alkalis, with the aid

of heat, dissolve it in small quantity; so likewise do *alkaline carbonates*, and without evolution of carbonic acid. Hot *alcohol* dissolves it readily. (Gericke.)

## ¶. Binitrosulphobenzene.

$$C^{24}N^2H^8S^2O^{12} = C^{24}X^2H^8(SO^2)^2.$$

GERICKE. *Ann. Pharm.* 100, 211.

Formed, together with the preceding compound, by the action of fuming nitric acid on sulphobenzene, or more abundantly by the action of a mixture of fuming nitric acid and oil of vitriol on the same compound. It is purified from the mononitrated compound by means of hot alcohol, in which it is but sparingly soluble.

Small white rhombic tables having a silky lustre. Melts at 164°, and solidifies in a crystalline mass on cooling. Sublimes without decomposition at 320°.

| | | | Gericke. |
|---|---|---|---|
| 24 C | 144 | 46·7 | 46·6 |
| 2 N | 28 | 9·1 | |
| 8 H | 8 | 2·6 | 3·0 |
| 2 S | 32 | 10·4 | 10·5 |
| 12 O | 96 | 31·2 | |
| $C^{24}N^2H^8S^2O^{12}$ | 308 | 100·0 | |

This formula being completely divisible by 2, it might appear as if the compound should rather be regarded as nitrosulphobenzene, $C^{12}XH^4SO^2$: but the double formula is justified, or rather necessitated, by the composition of the preceding compound, and also by that of the platinum-salt of the derived compound biamidosulphobenzene (p. 348), the formula of which does not admit of being halved.

Binitrosulphobenzene, *heated* on platinum-foil, burns with a sooty flame. It is not altered by caustic alkalis or alkaline carbonates, or by a mixture of hydrochloric acid and chlorate of potash. *Sulphide of ammonium* converts it into biamidosulphobenzene.

It is insoluble in water, soluble in strong *nitric acid*, but not in dilute acids. It dissolves but sparingly in *alcohol* and *ether*, even when heated. (Gericke.)

## ¶. Amidosulphobenzene.

$$C^{24}NH^{11}S^2O^4 = C^{24}AdH^9(SO^2)^2.$$

H. GERICKE. *Ann. Pharm.* 98, 389; 100, 210.

Formed by the action of sulphide of ammonium on nitrosulphobenzene (p. 346). The alcoholic solution of that compound mixed with sulphide

of ammonium assumes a blood-red colour, deposits sulphur, and is converted into amidosulphobenzene. On acidulating the liquid with hydrochloric acid, filtering and saturating with potash, the amidosulphobenzene is obtained in the form of a yellowish-white precipitate, which may be purified by repeated solution in hydrochloric acid and precipitating with potash.

Microscopic four-sided prisms, which decompose partially and acquire a darker colour when dried between paper. Heated on platinum foil, the compound melts and then burns away with a tranquil but very sooty flame. Dissolves sparingly in cold, readily in hot water, and in alcohol. Forms salts with acids.

*Hydrochlorate.* — Forms reddish, well-developed, four-sided prisms. Melts at about 90°, and solidifies in a gummy mass on cooling. Dissolves easily in water and alcohol, forming red solutions; the aqueous solution however is partially decomposed by heating, and if then treated with potash, gives off ammonia, and deposits a black flocculent body.

| | | | Gericke. |
|---|---|---|---|
| 24 C | 144·0 | 53·5 | 53·0 |
| N | 14·0 | 5·2 | |
| 12 H | 12·0 | 4·4 | 4·6 |
| Cl | 35·4 | 13·3 | 13·3 |
| 2 S | 32·0 | 11·8 | |
| 4 O | 32·0 | 11·8 | |
| $C^{24}NH^{11}S^2O^4,HCl$ | 269·4 | 100·0 | |

*Chloroplatinate.* $C^{24}AdH^9(SO^2)^2HCl,PtCl^2$. — Bichloride of platinum added to the solution of the hydrochlorate just described, forms a yellowish-brown precipitate, which does not appear crystalline under the microscope. It fuses readily when heated on platinum-foil. Insoluble in cold water, but dissolves with partial decomposition in hot water; cold alcohol dissolves it readily. Contains 24·9 p. c. platinum. (Gericke.)

## ¶. Biamidosulphobenzene.

$C^{24}N^2H^{12}S^2O^4 = C^{24}Ad^2H^8(SO^2)^2$.

GERICKE. *Ann. Pharm.* 100, 212.

Formed by the action of sulphide of ammonium on binitrosulphobenzene, $C^{24}X^2H^{12}(SO^2)$. Precipitated by potash from the hydrochloric acid solution, as a yellowish-white mass, which soon acquires a darker colour. Crystallises in small, four-sided prisms, which easily melt into a brownish mass. Dissolves sparingly in cold, readily in hot water and alcohol. Insoluble in alkalis, Forms salts with acids.

The *Hydrochlorate* crystallises in rhombic prisms of a reddish colour and longitudinally striated. Is not decomposed at 100°. Dissolves readily in water and alcohol.

| | | | | Gericke. |
|---|---|---|---|---|
| 24 C | 144·0 | 44·9 | | 45·1 |
| 2 N | 28·0 | 8·7 | | |
| 14 H | 14·0 | 4·4 | | 4·9 |
| 2 Cl | 70·8 | 22·0 | | 21·5 |
| 2 S | 32·0 | 10·0 | | |
| 4 O | 32·0 | 10·0 | | |
| $C^{24}N^2H^{12}S^2O^4,2HCl$ | 320·8 | 100·0 | | |

*Chloroplatinate.* $C^{24}(Ad)^2H^8(SO^2)^2, 2HCl, PtCl^2$. Brown-red, indistinctly crystalline precipitate, which is affected by heat and by solvents in the same manner as the platinum-salt of amidosulphobenzene. Contains 19·9 p. c. of platinum.

Amidosulphobenzene and biamidosulphobenzene treated with *iodide of ethyl* at 100°, yield merely red-brown, unctuous, uncrystallisable bodies, which do not form any very definite products with acids or when treated with oxide of silver. (Gericke.) ¶.

## Carbanilide.

$$C^{26}N^2H^{12}O^7 = C^{24}CyNH^{10},H^2O^2.$$

A. W. Hofmann. *Ann. Pharm.* 57, 266.

*Formation.* 1. When aniline is mixed with anilocyanic acid (p. 302). — 2. In the decomposition of anilocyanic acid by water (p. 302). — 3. In the decomposition of aniline by phosgene gas. — 4. In the decomposition of sulphocarbanilide (p. 351) by caustic potash. — 5. In the dry distillation of aniline-urea (p. 304), melanoximide (p. 367), or monoxalate of melaniline (p. 355).

*Preparation.* The crystalline mass obtained by passing phosgene gas not containing any free chlorine through aniline, is treated with boiling water to extract hydrochlorate of aniline, and the residue crystallised from alcohol. — 2. Vapour of cyanic acid is made to act on aniline, which must be kept hot, and the carbanilide separated from the aniline-urea. — 3. Aniline-urea is subjected to dry distillation. The needles which perhaps separate with a reddish tint are easily decolorised by animal charcoal.

*Properties.* White silky needles which melt at 205°, and distil without decomposition; they are inodorous at ordinary temperatures, but have a suffocating odour, like that of benzoic acid, when heated.

| | *Needles.* | | | Hofmann. |
|---|---|---|---|---|
| 26 C | 156 | 73·58 | | 73·48 |
| 2 N | 28 | 13·21 | | 13·07 |
| 12 H | 12 | 5·66 | | 5·84 |
| 2 O | 16 | 7·55 | | 7·61 |
| $C^{26}N^2H^{12}O^2$ | 212 | 100·00 | | 100·00 |

Metameric with the alkaline body, flavine.

*Decompositions.* 1. Carbanilide, rapidly *heated* in the moist state, yields carbonate of aniline and other products. — 2. By oil of vitriol, it is converted into carbonic and anilosulphuric acids :

$$C^{26}N^2H^{12}O^2 + 2HO + 4SO^3 = 2(C^{12}NH^7,2SO^3) + 2CO^2.$$

3. When boiled with potash-ley, and more quickly when boiled with hydrate of potash, it is resolved into aniline which volatilises, and a residue of carbonate of potash :

$$C^{26}N^2H^{12}O^2 + 2HO + 2KO = 2C^{12}NH^7 + 2(KO,CO^2).$$

It dissolves very sparingly in *water*, but abundantly in *alcohol* and *ether*. (Hofmann.)

## Sulphocarbanilide.

$$C^{26}N^2H^{12}S^2 = C^{24}CyNH^{10},H^2S^2.$$

A. W. Hofmann. (1846.) *Ann. Pharm.* 57, 266; 70, 142.
Laurent & Delbos. *N. J. Pharm.* 10, 309.
Laurent & Gerhardt. *N. Ann. Chim. Phys.* 22, 103; 24, 196.

*Formation.* 1. By the action of bisulphide of carbon upon aniline (p. 253), — 2. By the dry distillation of hydrosulphocyanate of aniline (p. 261). (Hofmann.)

*Preparation.* 1. A mixture of aniline and bisulphide of carbon (in equal parts, according to Laurent,) mixed with alcohol to accelerate the decomposition, is introduced into a flask provided with a cooling tube to cause the condensed vapours to flow back again, and heated for a day or two in the sand-bath till it no longer gives off sulphuretted hydrogen. The crystals thus produced are freed from excess of bisulphide of carbon by boiling, and recrystallised from alcohol. — 2. The liquid obtained by distilling hydrosulphate of ammonia is redistilled at a gentle heat, whereupon sulphide of ammonium and bisulphide of carbon pass over in two layers, while sulphocarbanilide remains. (Hofmann.) — 3. A mixture of aniline, sulphocyanide of potassium and sulphuric acid is distilled, and the distillate dissolved in boiling alcohol; it then, on cooling, yields sulphocarbanilide in colourless, nacreous, microscopic rhombic tables. (Laurent & Gerhardt.)

*Properties.* From the mixture of aniline and bisulphide of carbon: Crystalline scales (Hofmann); thick rhombic tables (Laurent); from alcohol : Iridescent laminæ having a strong lustre. (Hofmann.) Melts at 140° and distils without decomposition. Has a peculiar odour, especially when heated; in bitterness it exceeds all other known substances. (Hofmann.)

| | | | Hofmann. |
|---|---|---|---|
| 26 C | 156 | 68·42 | 68·28 |
| 2 N | 28 | 12·28 | 12·63 |
| 12 H | 12 | 5·26 | 5·28 |
| 2 S | 32 | 14·04 | 13·85 |
| $C^{26}N^2H^{12}S^2$ | 228 | 100·00 | 100·04 |

*Decompositions.* 1. The solution of sulphocarbanilide in oil of vitriol, when gently heated, rapidly gives off carbonic and sulphurous acids, and if then mixed with water, solidifies in the form of anilosulphuric acid, leaving a mother-liquor clouded by separation of sulphur:

$$C^{26}N^2H^{12}S^2 + 4HO + 4SO^3 = 2(C^{12}NH^7,2SO^3) + 2CO^2 + 2HS.$$

The sulphuretted hydrogen thus liberated is resolved, however, with the excess of oil of vitriol, into sulphurous acid and sulphur. — 2. Sulphocarbanilide fused with hydrate of potash gives off a large quantity of aniline and leaves carbonate of potash and sulphide of potassium:

$$C^{26}N^2H^{12}S^2 + 2HO + 4KO = 2C^{12}NH^7 + 2(KO,CO^2) + 2KS.$$

3. By alcoholic potash, it is slowly converted into sulphide of potassium and beautiful needles of carbanilide; and similarly, after being dissolved in alcohol, it is converted by mercuric oxide into black sulphide of mercury and carbanilide:

$$C^{26}N^2H^{12}S^2 + 2KO = 2KS + C^{26}N^2H^{12}O^2.$$

It is not decomposed by dilute acids or alkalies, or by alcoholic iodide, bromide, chloride, or cyanide of mercury.

*Combinations.* Sulphocarbanilide dissolves sparingly in *water,* but readily in *alcohol,* and crystallises from a hot-saturated alcoholic solution. (Hofmann.)

## Melaniline.

$$C^{26}N^3H^{13} = C^{24}CyNAdH^9,H^2.$$

A. W. Hofmann. (1848.) *Ann. Pharm.* 67, 129; 74, 8 and 17.

*Formation.* In the decomposition of aniline by chloride or bromide of cyanogen (p. 253).

*Preparation.* An excess of moistened cyanide of mercury is introduced into bottles filled with chlorine gas, and, as soon as the colour of the chlorine has completely disappeared (free chlorine would produce terchloraniline and terchlorocarbolic acid), the gaseous chloride of cyanogen is transferred from the bottles,—by means of an aspirator, through a tube adapted to the mouth of the bottle, and having a narrow tube next to it for admitting the air,—into a bottle containing dry aniline, which becomes very hot, acquires a dark colour, and thickens into a

crystalline mass. This mass is heated till the crystals melt, so that it may be completely saturated with chloride of cyanogen, which is absorbed rapidly at first, but afterwards more slowly as the liquid becomes thicker; hence to prevent loss of chloride of cyanogen, it is best to pass the gas finally through three test-tubes half filled with aniline. The clear brownish, non-crystalline, resinous mass, which is produced on the cooling of the aniline perfectly saturated with chloride of cyanogen, and consists of hydrochlorate of melaniline (together with a brown oil insoluble in hydrochloric acid, which forms in greater quantity as the chloride of cyanogen is more humid, and not at all if the gas has been previously passed over chloride of calcium), is dissolved in water, the solution being accelerated by addition of hydrochloric acid, and boiling; the liquid, which is filtered from the oil, precipitated by potash; and the white viscid precipitate, which immediately solidifies in the crystalline form (only after some time, however, if it contains undecomposed aniline,) is washed with cold water, till the whole of the chloride of potassium is removed, and purified by two crystallisations from a mixture of equal parts of alcohol and water, which yields the finest crystals.

*Properties.* White, hard, easily friable laminæ and broad needles, which float on water, but sink in the fused state, and between 120° and 130°, melt into a slightly coloured oil, which solidifies in a crystalline mass on cooling. Inodorous, but has a bitter persistent taste. Slightly blues reddened litmus, but does not change the colour of turmeric. Acquires a reddish tint when exposed to the air.

| | | | Hofmann. |
|---|---|---|---|
| 26 C | 156 | 73·93 | 73·75 |
| 3 N | 42 | 19·91 | 19·75 |
| 13 H | 13 | 6·16 | 6·41 |
| $C^{26}N^3H^{13}$ | 211 | 100·00 | 99·91 |

*Decompositions.* 1. Melaniline begins to decompose between 150° and 170°, giving off aniline and ammonia, which latter does not at first escape at 170°, but afterwards sparingly, and above 170° abundantly. The loss of aniline and ammonia amounts, after heating for several hours at 170°, to between 29·1 and 32·5 per cent.; and after further heating, whereupon ammonia escapes very abundantly, to between 35 and 37 per cent. If 3 At. melaniline give off 2 At. aniline when heated, the loss of aniline should be 29·38 per cent. The residue, which in the main may be regarded as $C^{54}N^7H^{25}$ (inasmuch as $3\,C^{26}N^3H^{13} - 2C^{12}NH^7 = C^{54}N^7H^{25}$), is a faintly coloured, transparent, brittle resinous mass, insoluble in water, sparingly soluble in alcohol, more easily soluble in oil of vitriol, and precipitated therefrom by water. When obtained with comparatively little loss of ammonia, and purified, it contains 72·29 p. c. C, and 5.65 H which agrees with the formula above given; but after greater loss of ammonia, it contains more than 74 p. c. C and not much more than 5 p. c. H. — 2. *Chlorine*-water added in very large excess to hydrochlorate of melaniline, completely precipitates the base in the form of a resinous mass of terchloromelaniline. If the chlorine-water be gradually added, till the turbidity thereby produced no longer disappears on agitation, the liquid filtered from the resinous precipitate (probably terchloromelaniline) con-

tains hydrochlorate of bichloromelaniline. — 3. When *bromine* is added to aqueous hydrochlorate of melaniline in the manner last described with reference to chlorine-water, the filtrate deposits, on evaporation, needles of hydrochlorate of bibromomelaniline; and the mother-liquor mixed with a larger quantity of bromine and evaporated, yields transparent, yellow, oily drops which crystallise on cooling, and probably consist of terbromomelaniline; for the red precipitate, resinous at first, but afterwards becoming crystalline, which their solution in hydrochloric acid forms with bichloride of platinum, contains 15 per cent. of platinum. — Bromine acting in excess on hydrochlorate of melaniline, forms a resinous substance still richer in bromine. — 4. Alcoholic *iodine* added in excess to hydrochlorate of melaniline, throws down nearly the whole as a black viscid mass, which, when the quantity of iodine is less, is precipitated in smaller amount, while undecomposed melaniline remains in solution. — 5. Fuming *nitric acid* suddenly mixed with an equal quantity of melaniline, produces great heat, rising even to explosion attended with slight fuming; and, when gradually added, produces, according to the duration of the action, orange-yellow crystals of an alkaloid with violet iridescence, and lemon-yellow prisms of an acid which forms scarlet salts with alkalis. Moderately strong nitric acid, added in great excess or heated, likewise exerts a decomposing action. — 6. *Cyanogen gas* passed through an alcoholic solution of melaniline, is abundantly absorbed; and this liquid, if then enclosed in a bottle, deposits bicyanomelaniline, the odour of cyanogen changing at the same time into that of hydrocyanic acid, while the brown mother-liquor contains other products of decomposition.

*Combinations.* Melaniline dissolves sparingly in cold *water*, somewhat more abundantly in hot water, and crystallises therefrom on cooling.

It dissolves readily in *bisulphide of carbon.*

*Salts of Melaniline.* — Melaniline, being but a weak base, does not precipitate ferric salts. It dissolves in acids very readily and with slight evolution of heat, and neutralises them completely. The salts are colourless or slightly coloured, mostly crystallisable, and taste very bitter; with firwood, chloride of lime and chromic acid, they do not exhibit the colouring produced by aniline-solutions. They are precipitated by ammonia and more completely by potash of soda (also by the carbonates, with evolution of carbonic acid, yielding a white, quickly crystallising precipitate), but not by aniline; neither does melaniline precipitate the aniline-salts.

*Phosphate of Melaniline.* — Very easily soluble in water, and crystallises therefrom but slowly.

*Sulphate of Melaniline.* — Rhombic laminæ united in stars. After drying at 100°, they contain 18·42 p. c. HO, $SO^3$, and are therefore $C^{26}N^3H^{13}$,HO,$SO^3$. The salt dissolves sparingly in cold, abundantly in hot water; dissolves also in alcohol and ether.

*Hydriodate of Melaniline.* — Concentrated hydriodic acid converts melaniline into an oil, which sinks to the bottom and gradually solidifies

in a crystalline mass. The salt, added to a solution of nitrate of silver, throws down 68·01 p. c. iodide of silver, and is therefore $C^{26}N^3H^{13}$, HI. It decomposes quickly on exposure to the air, with liberation of iodine. From a solution in boiling water, it separates on cooling in oily drops which afterwards solidify. It dissolves also in alcohol.

*Hydrobromate of Melaniline.* — Crystallises from water in stellate groups of needles, which yield 64·45 p. c. bromide of silver, and are therefore $C^{26}N^3H^{13}$, Br. Dissolves very readily in water, less readily in strong hydrobromic acid.

*Hydrochlorate of Melaniline.* — The aqueous solution does not yield crystals by spontaneous evaporation; when dried over oil of vitriol or in the water-bath, it dries up to a clear, slightly coloured gum, which crystallises very slowly. It is the most soluble in water of all the salts of melaniline.

*Hydrofluate of Melaniline.* — The solution of melaniline in weak hydrofluoric acid yields well developed crystals, having a faint reddish colour, somewhat soluble in water, less soluble in alcohol.

*Nitrate of Melaniline.* — Crystallises on cooling from the hot aqueous solution so completely, that the mother-liquor is but slightly clouded by potash, and not by ammonia. The needles assume a faint reddish tint by exposure to the air, but are otherwise permanent. They dissolve also in hot alcohol, but are nearly insoluble in ether.

| | | | Hofmann. |
|---|---|---|---|
| 26 C | 156 | 56·93 | 56·57 |
| 4 N | 56 | 20·44 | |
| 14 H | 14 | 5·11 | 5·17 |
| 6 O | 48 | 17·52 | |
| $C^{26}N^3H^{13},HO,NO^5$ | 274 | 100·00 | |

Melaniline, added to sulphate of copper, throws down a flocculent double compound.

With *corrosive sublimate* it forms a white precipitate, whose solution in water containing a few drops of hydrochloric acid, deposits long needles by spontaneous evaporation.

*Nitrate of Silver and Melaniline.* — Precipitated immediately on mixing the alcoholic solution of melaniline with aqueous nitrate of silver, as a white mass, which quickly agglutinates to a resin, and must be purified from free melaniline by trituration with alcohol; from a clear alcoholic mixture of melaniline and nitrate of silver, the salt separates after a few hours in hard crystalline geodes. Contains 17·61 p. c. silver, and is therefore $2C^{26}N^3H^{13} + AgO, NO^5$.

*Chloro-aurate of Melaniline.* — The deep yellow mixture of terchloride of gold, not too concentrated, and hydrochlorate of melaniline, becomes filled in the course of half an hour, after previous turbidity, with needles

having a golden lustre; in more concentrated solutions, a copious yellow precipitate is immediately produced. The salt dissolves sparingly in water, more freely in alcohol, very easily in ether, which, when shaken up with water in which the salt is suspended, rises to the surface of the water in the form of a deep yellow solution; and when the liquid is evaporated, the salt sinks to the bottom as an oil which solidifies in needles.

| | *Crystals.* | | | Hofmann. |
|---|---|---|---|---|
| 26 C | 156·0 | .... | 28·23 | ........ 28·61 |
| 3 N | 42·0 | .... | 7·60 | |
| 14 H | 14·0 | .... | 2·53 | ........ 2·67 |
| Au | 199·0 | .... | 36·01 | ........ 35·71 |
| 4 Cl | 141·6 | .... | 25·63 | |
| $C^{26}N^3H^{13},HCl,AuCl^3$ | 552·6 | .... | 100·00 | |

*Chloroplatinate of Melaniline.* — Precipitated on mixing hydrochlorate of melaniline with bichloride of platinum, first as a pale yellow crystalline powder, after which a portion separates in indistinct orange-yellow crystals, which are likewise obtained by dissolving the precipitate in hot water. Dissolves sparingly in alcohol, and still more sparingly in ether.

| | *Crystals.* | | | Hofmann. |
|---|---|---|---|---|
| 26 C | 156·0 | .... | 37·39 | ........ 37·21 |
| 3 N | 42·0 | .... | 10·07 | |
| 14 H | 14·0 | .... | 3·36 | ........ 3·65 |
| Pt | 99·0 | .... | 23·73 | ........ 23·48 |
| 3 C | 106·2 | .... | 25·45 | ........ 25·49 |
| $C^{26}N^3H^{13},HCl,PtCl^2$ | 417·2 | .... | 100·00 | |

*Oxalate of Melaniline.* — Melaniline forms crystals with excess of oxalic acid. These crystals melt when heated, give off, with violent ebullition, equal volumes of carbonic oxide and carbonic acid, smelling strongly of anilocyanic acid; yield a distillate of aniline and a beautiful crystalline sublimate of carbanilide; and leave a clear viscid mass, which on cooling solidifies to a resin resembling that produced from heated melaniline (p. 352). The salt dissolves sparingly in cold water or alcohol, readily in boiling water or alcohol, but is nearly insoluble in ether. The crystals contain 29·73 p. c. $C^4H^2O^8$.

| | *Crystals.* | | | Hofmann. |
|---|---|---|---|---|
| 30 C | 180 | .... | 59·80 | ........ 60·35 |
| 3 N | 42 | .... | 13·95 | |
| 15 H | 15 | .... | 4·98 | ........ 5·20 |
| 8 O | 64 | .... | 21·27 | |
| $C^{26}N^3H^{13},C^4H^2O^8$ | 301 | .... | 100·00 | |

Melaniline dissolves readily in *wood-spirit, alcohol, ether, acetone,* and in *oils* both *fixed* and *volatile.* (Hofmann.)

## Biniodomelaniline.

$$C^{26}N^3H^{11}I^2 = C^{24}CyNAdI^2H^7,H^2.$$

A. W. Hofmann. (1848.) *Ann. Pharm.* 67, 152; *Chem. Soc. Qu. J.* 1, 303.

When chloride of cyanogen is passed through an ethereal solution of iodaniline, a crystalline precipitate of hydrochlorate of iodaniline is first formed; but if the passage of the gas be continued the crystals disappear and the entire mass changes into a transparent resin of hydrochlorate of biniodomelaniline (p. 277), which slowly becomes crystalline. From this compound, potash throws down the base in the form of a white body, which crystallises indistinctly from alcohol.

| | *Biniodomelaniline.* | | Hofmann. |
|---|---|---|---|
| 26 C | 156 | 33·84 | 33·90 |
| 3 N | 42 | 9·11 | |
| 2 I | 252 | 54·66 | |
| 11 H | 11 | 2·39 | 2·71 |
| $C^{26}N^3H^{11}I^2$ | 461 | 100·00 | |

*Hydrochlorate.* — Dissolves sparingly in water and separates from the boiling solution on cooling in oily drops, which very slowly change into white crystalline stars.

*Chloroplatinate.* — Not very crystalline.

| | | | Hofmann. |
|---|---|---|---|
| 26 C | 156·0 | 23·38 | 23·20 |
| 3 N | 42·0 | 6·29 | |
| 2 I | 252·0 | 37·77 | |
| 12 H | 12·0 | 1·80 | 2·11 |
| Pt | 99·0 | 14·84 | 14·67 |
| 3 Cl | 106·2 | 15·92 | |
| $C^{62}N^3I^2H^{11},HCl + PtCl^2$. | 667·2 | 100·00 | |

## Bibromomelaniline.

$$C^{26}N^3Br^2H^{11} = C^{24}CyNAdBr^2H^7,H^2.$$

A. W. Hofmann. (1848.) *Ann. Pharm.* 67, 148; *Chem. Soc. Qu. J.* 1, 299.

An aqueous solution of hydrochlorate of melaniline mixed with bromine in small portions, till the turbidity begins to be permanent, yields, when filtered, evaporated, and cooled, stellate groups of hydrobromate of bibromomelaniline (p. 353), which, when dissolved in water, form with

ammonia a white crystalline precipitate, which crystallises from hot alcohol in white scales. The base tastes very bitter in its solutions.

| | *Crystals.* | | | Hofmann. |
|---|---|---|---|---|
| 26 C | 156 | .... | 42·28 | 42·37 |
| 3 N | 42 | .... | 11·38 | |
| 2 Br | 160 | .... | 43·36 | |
| 11 H | 11 | .... | 2·98 | 2·80 |
| $C^{26}N^3Br^2H^{11}$ | 369 | .... | 100·00 | |

The compound heated above its melting point, gives off pure bromaniline in the form of a colourless distillate, which solidifies in a yellowish crystalline mass, leaving a resinous mass similar to the residue obtained in the distillation of melaniline (p. 352.)

Bibromomelaniline is nearly insoluble in water, but dissolves in alcohol and ether.

Its *hydrochlorate* crystallises in white silky needles grouped in stars. These crystals, when immersed in a small quantity of boiling water, melt into an oil which solidifies in the crystalline form on cooling; they dissolve sparingly in water, and contain 9·19 per cent. of hydrochloric acid; hence they are $C^{26}N^3Br^2H^{11},HCl$.

The hot-saturated solution of the hydrochlorate forms with bichloride of platinum, an orange-yellow precipitate, which, on cooling crystallises in golden-yellow scales, nearly insoluble in water, sparingly soluble in ether, somewhat more in alcohol. (Hofmann.)

| | *Platinum-salt.* | | | Hofmann. |
|---|---|---|---|---|
| 26 C | 156·0 | .... | 27·12 | 27·45 |
| 3 N | 42·0 | .... | 7·32 | |
| 2 Br | 160·0 | .... | 27·81 | |
| 12 H | 12·0 | .... | 2·08 | 2·32 |
| Pt | 99·0 | .... | 17·21 | 17·11 |
| 3 Cl | 106·2 | .... | 18·46 | |
| $C^{26}N^3Br^2H^{11},HCl + PtCl^2$ | 575·2 | .... | 100·00 | |

## Bichloromelaniline.

$$C^{24}N^3Cl^2H^{11} = C^{24}CyNAdCl^2H^7,H^2.$$

A. W. Hofmann. (1848.) *Ann. Pharm.* 67, 146; *Chem. Soc. Qu. J.* 1, 298.

When chlorine-water is gradually added to hydrochlorate of melaniline, till the turbidity no longer disappears on agitation (p. 352), the filtrate evaporated and cooled, yields hydrochlorate of bichloromelaniline in white stellate needles, or by further evaporation, as a yellowish oil which solidifies in the crystalline form. From the solution of this salt in water, in which it is sparingly soluble, whereas it dissolves more readily in alcohol and still more in ether, ammonia precipitates the base in snow-white flakes, which separate from the alcoholic solution in hard crystalline laminæ.

*Platinum-salt.*—The hydrochlorate mixed with bichloride of platinum, yields an orange-yellow, crystalline powder which must be washed with ether.

| | | | | | | Hofmann. |
|---|---|---|---|---|---|---|
| 26 C | 156 | .... | 32·10 | ........ | 32·06 |
| 3 N | 42 | .... | 8·64 | | |
| 12 H | 12 | .... | 2·47 | ........ | 2·54 |
| Pt | 99 | .... | 20·37 | ........ | 20·26 |
| 5 Cl | 177 | .... | 36·42 | | |
| $C^{26}N^3Cl^2H^{11},HCl + PtCl^2$ | 486 | .... | 100·00 | | |

The resinous mass precipitated by mixing hydrochlorate of melaniline with a very large excess of chlorine water, which hardens after a while into an amorphous solid, exhibits a neutral reaction, and is insoluble in water but soluble in alcohol, is probably terchloromelaniline, $C^{26}N^3Cl^3H^{10}$. (Hofmann.)

## Binitromelaniline.

$$C^{26}N^5H^{11}O^8 = C^{24}CyNAdX^2H^7,H^2.$$

A. W. HOFMANN. (1848.) *Ann. Pharm.* 67, 156; *Chem. Soc. Qu. J.* 1, 305.

*Formation.* From nitraniline and chloride of cyanogen (p. 290).

*Preparation.* Gaseous chloride of cyanogen is passed through a solution of nitraniline in ether till the ether is nearly evaporated; the remaining crystalline mixture of undecomposed nitraniline, hydrochlorate of binitromelaniline, and indifferent yellowish needles, heated with gradual addition of water, till the mass, which at first melts into a brown oil, is almost entirely dissolved; the liquid cooled till the yellowish needles separate; the colourless filtrate containing hydrochlorate of binitromelaniline, mixed with ammonia which throws down the binitromelaniline, as a quickly crystallising, sulphur-yellow mass; and this precipitate freed from nitraniline, with which it is generally mixed, by boiling with water.

*Properties.* After precipitation by ammonia or potash: scaly crystalline mass, of a much paler yellow colour than nitraniline. Precipitated from alcohol by water: Golden-yellow crystalline mass, and short flat microscopic needles. Crystallised from ether by spontaneous evaporation: Larger needles.

| | | | | | Hofmann. |
|---|---|---|---|---|---|
| 26 C | 156 | .... | 51·83 | ........ | 51·71 |
| 5 N | 70 | .... | 23·25 | | |
| 11 H | 11 | .... | 3·65 | ........ | 3·96 |
| 8 O | 64 | .... | 21·27 | | |
| $C^{26}N^5H^{11}O^8$ | 301 | .... | 100·00 | | |

*Decompositions.* Binitromelaniline when heated gives off a yellow vapour, which condenses in brown oily drops chiefly consisting of nitraniline and gradually crystallising, and leaves in the retort a brown resinous mass.

*Combinations.* Binitromelaniline is insoluble in water, even at the boiling heat.

*Hydrochlorate of Binitromelaniline.* — Flat shining needles, sparingly soluble in water; they contain 10·82 p. c. hydrochloric acid, and are therefore $C^{26}N^5H^{11}O^8,HCl$.

*Chloroplatinate of Binitromelaniline.* — The solution of the hydrochlorate forms with bichloride of platinum, a yellow crystalline precipitate, which contains 19·58 p.c. platinum, and is therefore $C^{26}N^5H^{11}O^8,HCl,PtCl^2$. It burns with slight detonation when heated, and dissolves sparingly in water and alcohol, but not in ether.

The *sulphate* forms white crusts which dissolve readily in water. — The *nitrate* is sparingly soluble. — The *oxalate* forms easily soluble crystalline grains.

Binitromelaniline dissolves sparingly in *alcohol* and still less in *ether*. (Hofmann.)

## Cyaniline.

$$C^{28}N^4H^{14} = C^{24}Cy^2Ad^2H^8,H^2.$$

HOFMANN. *Ann. Pharm.* 66, 129; 73, 180; *Chem. Soc. Qu. J.* 1, 160; 2, 300.

*Formation* (pp. 252, 253).

*Preparation.* Cyanogen gas is passed through a solution of aniline in a six-fold quantity of alcohol, till the liquid smells strongly of it, but not longer; and the resulting crystals are freed from the mother-liquor, which colours them reddish yellow, either by repeated washing with cold alcohol, or by washing them twice with that liquid and subsequently dissolving them in dilute sulphuric acid, filtering from a red crystalline powder, precipitating the pale yellow filtrate by ammonia, and crystallising the pale yellow pulverulent precipitate once, twice, or three times from a large quantity of boiling alcohol, till colourless laminæ are obtained.

*Properties.* Colourless, silvery, iridescent laminæ, which do not volatilise without decomposition, even in company with vapour of water; they melt between 210° and 220°, and solidify in the crystalline form on cooling; they are heavier than water; inodorous and tasteless; neutral. The acid solutions of this base do not colour firwood yellow; neither do they turn blue in contact with chloride of lime, or give the precipitates of aniline with chromic acid.

| | Crystals. | | Hofmann. |
|---|---|---|---|
| 28 C | 168 | 70·59 | 70·60 |
| 4 N | 56 | 23·53 | 23·77 |
| 14 H | 14 | 5·88 | 6·24 |
| $C^{28}N^4H^{14}$ | 238 | 100·00 | 100·61 |

Hofmann adopts the simple formula $C^{14}N^2H^7$; the doubling of this formula to $C^{28}N^4H^{14}$, first proposed by Laurent & Gerhardt (*N. J. Pharm.* 14, 307; *Compt. chim.* 1849, 76 and 168), is sanctioned by the unevenness of the simple formula, and the non-volatility of the compound.

*Decompositions.* 1. Cyaniline, at a temperature a little above its melting point, turns brown, chars, and gives off aniline together with hydrocyanate of ammonia.—2. *Bromine* becomes strongly heated in contact with cyaniline, and perhaps forms at first, bromocyaniline, which however is ultimately converted into terbromaniline. — 3. The violet solution of cyaniline in *oil of vitriol*, gives off, when slightly heated, a mixture of carbonic acid and carbonic oxide, which latter is more and more replaced by sulphurous acid as the heat increases; and, the liquid on cooling, solidifies in a crystalline mass consisting of sulphate of ammonia and anilosulphuric acid:

$$C^{28}N^4H^{14} + 8HO + 6SO^3 = 2(C^{12}NH^7,2SO^3) + 2CO + 2CO^2 + 2(NH^4O,SO^3).$$

4. The solution in dilute hydrochloric (or dilute sulphuric acid) soon assumes a deep yellow colour, and when evaporated over the water-bath, gives off an odour of anilocyanic acid, and leaves a white crystalline mass, from which sal-ammoniac and hydrochlorate of aniline are extracted by cold water, and afterwards oxamide and oxanilamide (p. 312) by boiling water, whilst oxanilide is left undissolved in quantity equal to that of the oxamide and the oxanilamide. In this case, two decompositions appear to take place simultaneously:

$$(1).\ C^{28}N^4H^{14} + 4HO + 2HCl = 2NH^4Cl + \underbrace{C^{28}N^2H^{12}O^4}_{\text{oxanilide.}}$$

$$(2).\ C^{28}N^4H^{14} + 4HO + 2HCl = \underbrace{C^4N^2H^4O^4}_{\text{oxamide.}} + \underbrace{2C^{12}NH^8Cl.}_{\text{hydrochlorate of aniline.}}$$

At the moment of formation (but not afterwards) the oxanilide and oxamide are partly converted into oxanilamide:

$$C^{28}N^2H^{12}O^4 + C^4N^2H^4O^4 = 2C^{16}N^2H^8O^4.$$

[Perhaps also, altogether:

$$4C^{28}N^4H^{14} + 16HO + 8HCl = 4NH^4Cl + 4C^{12}NH^8Cl + C^4N^2H^4O^4 + 2C^{16}N^2H^8O^4 + C^{28}N^2H^{12}O^4].$$

Cold dilute acids gradually eliminate aniline and give off the odour of anilocyanic acid. — 5. Cyaniline is not altered by boiling aqueous or alcoholic potash, but by hydrate of potash in the state of fusion, it is converted into ammonia, aniline, hydrogen gas, and carbonate of potash:

$$C^{28}N^4H^{14} + 8HO + 4KO = 2H + 2NH^3 + 2C^{12}NH^7 + 4(KO,CO^2).$$

*Combinations.* Cyaniline is insoluble in water and dissolves but sparingly in *bisulphide of carbon.*

*Salts of Cyaniline.* — These salts must be brought to the solid state as quickly as possible, before they decompose. They are not produced by passing cyanogen gas through alcoholic solutions of aniline-salts. According to the formula $C^{28}N^4H^{14}$, they must be regarded as biacid salts.

*Sulphate of Cyaniline.* — Very soluble, decomposes by evaporation, like the hydrochlorate.

*Hydriodate of Cyaniline.* — Resembles the hydrochlorate, but quickly deposits iodine on exposure to the air.

*Hydrobromate of Cyaniline.* — Cyaniline is dissolved in boiling dilute hydrobromic acid, and the filtrate immediately mixed with an equal quantity of concentrated hydrobromic acid, which separates crystals, to be washed, first with concentrated hydrobromic acid, then with ether. The salt is very much like the hydrochlorate of cyaniline.

| | *Crystals.* | | Hofmann. |
|---|---|---|---|
| 28 C | 168 | 42 | 42·33 |
| 4 N | 56 | 14 | |
| 16 H | 16 | 4 | 4·05 |
| 2 Br | 160 | 40 | 39·28 |
| $C^{28}N^4H^{14},2HBr$ | 400 | 100 | |

*Hydrochlorate of Cyaniline.*—The boiling yellow solution of cyaniline in boiling dilute hydrochloric acid, is filtered hot and immediately mixed with an equal quantity of fuming hydrochloric acid, which decolorises it, and soon causes the separation of a large quantity of colourless crystals, which must be washed with hydrochloric acid and then with ether. These crystals, which have a very sweet taste, are permanent when dry, but decompose in the moist state, becoming at the same time insoluble in water. Their aqueous solution yields by evaporation, the same products of decomposition as the direct solution of cyaniline in dilute hydrochloric acid (p. 360). Aniline added to the aqueous solution of the crystals, precipitates the cyaniline as the weaker base, and acids throw down the crystals in their original state. The crystals dissolve with great facility in water and in alcohol.

| | *Crystals.* | | Hofmann. |
|---|---|---|---|
| 28 C | 168·0 | 54·05 | 54·02 |
| 4 N | 56·0 | 18·02 | |
| 16 H | 16·0 | 5·15 | 5·45 |
| 2 Cl | 70·8 | 22·78 | 22·82 |
| $C^{28}N^4H^{14},2HCl$ | 310·8 | 100·00 | |

*Nitrate of Cyaniline.* — The solution of cyaniline in boiling dilute nitric acid, yields on cooling, white needles, which may be crystallised without decomposition from boiling water, dissolve sparingly in cold water, and to a still less amount in alcohol and ether.

| | *Crystals.* | | Hofmann. |
|---|---|---|---|
| 28 C | 168 | 46·16 | 46·38 |
| 6 N | 84 | 23·07 | |
| 16 H | 16 | 4·40 | 4·63 |
| 12 O | 96 | 26·37 | |
| $C^{28}N^4H^{14},2HO,2NO^5$ | 364 | 100·00 | |

Nitrate of cyaniline forms a crystallisable double salt with *nitrate of silver*.

*Chloro-aurate of Cyaniline.* — The solution of cyaniline in hydrochloric acid or in alcohol, forms with terchloride of gold, which, in the former case, should not contain too much free hydrochloric acid, an orange-yellow precipitate, which, after washing with water and drying at 100°, contains 42·92 per cent. of gold, and is therefore $C^{28}N^4H^{14},2HCl,2AuCl^3$. It dissolves very readily in ether. When dissolved in ether in the moist state, it is completely converted, as the ether evaporates, into the crystallisable chloro-aurate of aniline no longer soluble in ether, and into other products; if dissolved in the dry state, it leaves a mixture of this product of decomposition with a few crystals of the unaltered gold-salt.

*Chloroplatinate of Cyaniline.* — Tolerably strong hydrochloric acid saturated at the boiling heat with cyaniline, and mixed with a concentrated solution of bichloride of platinum, yields on cooling, orange-yellow needles which must be washed with ether. From their solution in water or alcohol, they can no longer be obtained in the crystalline form. The aqueous solution becomes turbid when evaporated, and deposits crystals, first of chloroplatinate of aniline, then of chloroplatinate of ammonium, and yields also other products of decomposition.

| | | | Hofmann. |
|---|---|---|---|
| 28 C | 168·0 | 25·83 | 25·93 |
| 4 N | 56·0 | 8·61 | |
| 16 H | 16·0 | 2·46 | 2·50 |
| 2 Pt | 198·0 | 30·44 | 30·32 |
| 6 Cl | 212·4 | 32·66 | |
| $C^{28}N^4H^{14},2HCl + 2PtCl^2$ | 650·4 | 100·00 | |

*Oxalate of Cyaniline.* — Behaves like the sulphate.

Cyaniline dissolves with difficulty in *wood-spirit, alcohol, ether, benzene,* and in *oils* both *fixed* and *volatile.* (Hofmann.)

## Bicyanomelaniline.

$C^{10}N^5H^{13} = C^{24}Cy^3Ad^2H^7,H^2$.

A. W. Hofmann. (1848.) *Ann. Pharm.* 67, 160; 74, 1.

*Formation* (p. 353).

*Preparation.* Cyanogen gas is passed to saturation through alcohol saturated in the cold with cyanogen gas; the solution set aside in a closed vessel, for some hours, till it solidifies into a mass of yellowish silky needles; the brown mother-liquor drained from these crystals, and the crystals washed with cold alcohol, and recrystallised three times from hot alcohol.

*Properties.* Needles having a very pale yellow colour, and not volatile without decomposition.

| | | *Needles.* | | | Hofmann. |
|---|---|---|---|---|---|
| 30 C | 180 | .... | 68·44 | ........ | 68·34 |
| 5 N | 70 | .... | 26·62 | | |
| 13 H | 13 | .... | 4·94 | ........ | 5·13 |
| $C^{30}N^5H^{13}$ | 263 | .... | 100·00 | | |

*Decompositions.* 1. Bicyanomelaniline when heated, gives off aniline and hydrocyanate of ammonia, and leaves a resin which becomes carbonised at a higher temperature.—2. Its pale yellow solution in moderately strong hydrochloric acid (from which at the first moment, ammonia throws down unaltered bicyanomelaniline) becomes coloured in a few minutes (instantly if somewhat concentrated or if heat is applied), and gradually deposits melanoximide (p. 266), in the form of a pale yellow crystalline powder, while the mother-liquor retains sal-ammoniac, the nitrogen in which amounts to 10·97 per cent. of the bicyanomelaniline employed :

$$C^{26}N^5H^{13} + 2HCl + 4HO = C^{30}N^3H^{11}O^4 + 2NH^4Cl.$$

Other acids, even vegetable acids, act like hydrochloric acid, the more quickly as they are more concentrated.—3. The boiling alcoholic solution of bicyanomelaniline mixed with excess of hydrochloric acid, acquires a transient yellow colour, and on cooling deposits white needles, sal-ammoniac being formed at the same time and the liquid losing its colour.

*Combinations.* Bicyanomelaniline is insoluble in water.—It dissolves in cold dilute *acids*, even in vegetable acids, and thence appears to be a weak base; but in consequence of its rapid conversion into melanoximide and ammoniacal salt, which does not allow the precipitation of unaltered bicyanomelaniline by potash or ammonia, excepting at the first instant after solution, it is impossible to obtain crystallised salts of this base.

Bicyanomelaniline dissolves with tolerable facility in *alcohol.*

## Chlorocyanilide.

$$C^{30}N^5ClH^{12} = C^{24}Cy^3Ad^2H^7,HCl. ?$$

LAURENT. (1842.) *N. Ann. Chim. Phys.* 22, 97; also *J. pr. Chem.* 44, 157; abstr. *N. J. Pharm.* 10, 308.

*Formation and Preparation.* Solid chloride of cyanogen (ix, 463) in the state of powder is gradually introduced into a flask containing aniline dissolved in lukewarm water and the requisite quantity of alcohol; and the chlorocyanilide which falls down as a white powder,

is washed with water and alcohol successively, after the liquid which contains the hydrochlorate of aniline has been decanted :

$$4C^{12}NH^7 + C^6N^3Cl^3 = C^{30}N^5ClH^{12} + 2(C^{12}NH^7,HCl).$$

Similar therefore to the formation of chlorocyanamide (ix, 478).

*Properties.* Crystallises from alcohol on cooling, in white, highly lustrous, somewhat elongated laminæ, and after fusion in radiating needles. Not volatile without decomposition.

| | | *Crystals.* | | Laurent. |
|---|---|---|---|---|
| 30 C | 180·0 | 60·52 | | 60·80 |
| 5 N | 70·0 | 23·54 | | 23·28 |
| Cl | 35·4 | 11·90 | | 11·80 |
| 12 H | 12·0 | 4·04 | | 4·12 |
| $C^{30}N^5ClH^{12}$ | 297·4 | 100·00 | | 100·00 |

*Decompositions.* 1. Heated somewhat above its melting point, it gives off 11·8 per cent. of hydrochloric acid, becoming less fluid, and ultimately leaves a greenish, transparent, vesicular residue, which must be $C^{30}N^5H^{11}$ [$C^{24}Cy^3NAdH^7,H^2$ Gm.—Hofmann (*Ann. Pharm.* 74, 21) regards it as a compound of his aniline-mellone $C^{18}N^4H^4$ with aniline : $C^{30}N^5H^{11} = C^{18}N^4H^4 + C^{12}NH^7$]. — 2. It dissolves slowly in boiling potash as chloride of potassium and *anilinammeline*, $C^{30}N^5H^{13}O^2$ :

$$C^{30}N^5ClH^{12} + HO + KO = C^{30}N^5H^{13}O^2 + KCl.$$

By neutralising the cooled potash solution with nitric acid, the anilinammeline is obtained as a white flocculent precipitate, which is insoluble in ammonia, but dissolves in hot weak nitric acid, and separates in the form of a jelly on cooling. It contains 62·6 p. c. carbon (somewhat too little), and 4·6 hydrogen. (Laurent.) — [Probably = $C^{24}Cy^3Ad^2H^7,H^2O^2$, Gm.]

## Oxanilide.

$$C^{28}N^2H^{12}O^4 = C^{24}(C^4HO^2)NAdH^9,O^2. ?$$

GERHARDT. (1845.) *N. Ann. Chim. Phys.* 14, 120 and 15, 88; also *N. J. Pharm.* 8, 56; also *J. pr. Chem.* 35, 295. — *N. J. Pharm.* 9, 406; also *J. pr. Chem.* 39, 298.
A. W. HOFMANN. *Ann. Pharm.* 65, 56; 73, 181; 74, 35.

*Oxanilid, Anilide oxalique.*

*Formation.* 1. (p. 262.) — 2. In the decomposition of cyaniline by dilute hydrochloric or sulphuric acid. (Hofmann.)

*Preparation.* 1. Binoxalate of aniline is heated to between 160° and 180°, till the evolution of gas ceases, and the solidified mass is exhausted with cold alcohol, which dissolves formanilide and leaves oxanilide undis-

solved. (Gerhardt.) — 2. The solution of cyaniline in excess of dilute hydrochloric acid is evaporated over the water-bath; the dry residue treated with cold water to remove sal-ammoniac and hydrochlorate of aniline, then with boiling water to dissolve oxamide and oxanilamide; and the oxanilide which remains undissolved, is purified by solution in benzene, filtration, and evaporation, and by washing the crystals with alcohol. (Hofmann.)

*Properties.* White nacreous scales, which melt at 245° and solidify in a radiating mass on cooling; they boil at 320°, giving off a sharp vapour like that of benzoic acid, and distilling for the most part without decomposition, and sublime at a gentle heat in iridescent laminæ.

| | | | Gerhardt. | Hofmann. |
|---|---|---|---|---|
| 28 C | 168 | 70·00 | 69·63 | 69·60 |
| 2 N | 28 | 11·67 | 12·40 | |
| 12 H | 12 | 5·00 | 5·13 | 5·00 |
| 4 O | 32 | 13·33 | 12·84 | |
| $C^{28}N^2H^{12}O^4$ | 240 | 100·00 | 100·00 | |

*Decompositions.* 1. Oxanilide subjected to rapid *distillation*, yields a small quantity of oil containing a trace of anilocyanic acid, which gives it a powerful odour. — 2. *Bromine* acts violently upon oxanilide, giving off hydrobromic acid and forming a substance which dissolves in ether and crystallises therefrom. (Gerhardt.) — 3. Hot *nitric acid* gives off red vapours. (Gerhardt.) Aqueous chromic acid and other dilute acids do not act upon oxanilide, even when heated. — 4. The solution of oxanilide in warm *oil of vitriol* effervesces when strongly heated, giving off carbonic oxide and carbonic acid in equal volumes; it then turns slightly brown, and on the addition of a small quantity of water, deposits a large quantity of anilosulphuric acid in the form of a white crystalline powder (Gerhardt):

$$C^{28}N^2H^{12}O^4 + 2HO + 4SO^3 = 2(C^{12}NH^7,2SO^3) + 2CO + 2CO^2.$$

5. Oxanilide *distilled* with anhydrous phosphoric acid or chloride of zinc, gives off carbonic oxide and carbonic acid, and is almost completely carbonized; nevertheless, especially with phosphoric acid, the oil which smells of anilocyanic acid passes over, together with sublimed carbanilide, in larger quantity than when the oxanilide is distilled alone. (Hofmann.) — 6. Vapour of oxanilide passed over red-hot *lime*, yields a body which may be regarded as $C^{28}N^2H^8$. (Hofmann.) — 7. Oxanilide heated with dry lime gives off aniline, and becomes partially carbonised, and sometimes heated to redness. (Gerhardt.) Anhydrous baryta eliminates scarcely any thing but aniline. (Hofmann.) Oxanilide heated with potash-lime, hydrate of potash, or concentrated (not with dilute) potash-ley, is resolved into a distillate of aniline and a residue of oxalate of potash. (Gerhardt.)

*Combinations.* Oxanilide does not dissolve in water or in dilute sulphuric acid, even at the boiling heat. (Gerhardt.)

Oxanilide dissolves in slightly heated *oil of vitriol*, and is precipitated therefrom without alteration by water. (Gerhardt.)

It is insoluble in cold *alcohol*, sparingly soluble in boiling alcohol whence it crystallises in micaceous scales. (Gerhardt.)

It dissolves with greater facility in *benzene*. (Hofmann.) — Insoluble in ether. (Gerhardt.)

## Melanoximide.

$C^{30}N^3H^{11}O^4 = C^{24}(C^4HO^2)CyNAdH^8,O^2$. ?

A. W. Hofmann. (1848.) *Ann. Pharm.* 67, 160; 74, 2; *Chem. Soc. Qu. J.* 2, 307.

*Formation.* In the decomposition of bicyanomelaniline by dilute acids (p. 363).

*Preparation.* Bicyanomelaniline is dissolved in moderately strong hydrochloric acid, and the gradually precipitated crystalline powder (or slowly crystallising resin) washed with water.

*Properties.* Pale yellow, indistinctly crystalline powder.

| | | | Hofmann. |
|---|---|---|---|
| 30 C | 180 | 67·92 | 67·52 |
| 3 N | 42 | 15·85 | 15·40 |
| 11 H | 11 | 4·15 | 4·12 |
| 4 O | 32 | 12·08 | 12·96 |
| $C^{30}N^3H^{11}O^4$ | 265 | 100·00 | 100·00 |

May be regarded as acid oxalate of melaniline — 4 At. water = $C^{26}N^3H^{13},C^4H^2O^8 - 4HO$.

*Decompositions.* 1. Melanoximide melts when *heated*, giving off a large quantity of carbonic oxide, together with a small quantity of carbonic acid (probably resulting from a secondary decomposition), and with the strong-smelling vapour of anilocyanic acid, about 10 per cent. of which condenses in the form of a yellowish liquid; at a stronger heat, the melanoximide ultimately yields carbanilide sublimed in radiating crystals, and leaves a pale yellow transparent mass of resin, like that obtained from heated melaniline (p. 352). This resinous residue, after moderate heating, has the composition A, after stronger heating, the composition B;

| A. | | | Hofmann. |
|---|---|---|---|
| 56 C | 336 | 71·04 | 71·28 |
| 7 N | 98 | 20·72 | 19·77 |
| 23 H | 23 | 4·86 | 4·14 |
| 2 O | 16 | 3·38 | 4·81 |
| $C^{56}N^7H^{23}O^2$ | 473 | 100·00 | 100·00 |

| B. | | | Hofmann. |
|---|---|---|---|
| 30 C | 180 | 68·97 | 67·27 |
| 5 N | 70 | 26·82 | |
| 11 H | 11 | 4·21 | 4·54 |
| $C^{30}N^5H^{11}$ | 261 | 100·00 | |

Perhaps the melanoximide first gives off 2 At. carbonic oxide and yields a melanocarbimide, $C^{28}N^3H^{11}O^2$:

$$C^{30}N^3H^{11}O^4 = 2CO + C^{28}N^3H^{11}O^2.$$

By the further action of the heat, 3 At. melanocarbimide are then resolved into 2 At. anilocyanic acid and the residue A:

$$3C^{28}N^3H^{11}O^2 = 2C^{14}NH^5O^2 + C^{56}N^7H^{23}O^2.$$

and lastly, at a stronger heat, residue A gives off carbanilide, part of which may be produced from anilocyanic acid and water, and leaves the residue B:

$$C^{56}N^7H^{23}O^2 = C^{26}N^2H^{12}O^2 + C^{30}N^5H^{11}.$$

2. Melanoximide is but slightly decomposed by dilute sulphuric or hydrochloric acid; but when dissolved in alcohol and boiled with concentrated hydrochloric acid, it is resolved into oxalic acid, melaniline, and needles not yet fully examined, the solution at the same time acquiring a deep yellow colour, and emitting a powerful odour of anilocyanic acid. — 3. Its alcoholic solution solidifies in contact with *ammonia* or *potash*, either of which takes up a large quantity of oxalic acid, forming crystals of melaniline; and a similar decomposition takes place gradually in its solution in aqueous ammonia or potash, especially when concentrated.

*Combinations.* Melanoximide does not dissolve in water or in aqueous acids.

In aqueous *ammonia* or *potash* it dissolves at first without decomposition, and may be precipitated from the solution by acids; afterwards decomposition (3) takes place.

Its solution in weak alcohol forms with nitrate of *silver*, especially on addition of a small quantity of ammonia, a light yellow amorphous precipitate, containing from 25·4 to 28·57 and 30·5 per cent. of silver.

It dissolves sparingly in boiling *alcohol*, and crystallises therefrom in crusts. (Hofmann.)

## Succinanilide.

$$C^{32}N^2H^{16}O^4 = C^{24}(C^8H^5O^2)NAdH^9,O^2.\ ?$$

LAURENT & GERHARDT. (1848.) *N. Ann Chim. Phys.* 24, 182.

Succinic acid mixed in a flask with excess of aniline, and heated for ten minutes to the melting point, till water and the excess of aniline are driven off, yields a liquid which on cooling solidifies in spherically grouped needles, and from which boiling water extracts succinanil, while succinanilide remains undissolved and may be purified by crystallisation from alcohol.

It crystallises from the alcoholic solution in slender needles which melt at 220°.

| | | | Laurent & Gerhardt. |
|---|---|---|---|
| 32 C | 192 | 71·64 | 71·5 |
| 2 N | 28 | 10·45 | |
| 16 H | 16 | 5·97 | 6·2 |
| 4 O | 32 | 11·94 | |
| $C^{32}N^2H^{16}O^4$ | 268 | 100·00 | |

When fused at a gentle heat with hydrate of potash, it immediately gives off aniline.

It is insoluble in water, but dissolves readily in *alcohol* and *ether*. (Laurent & Gerhardt.)

## ¶. Malanilide.

$$C^{32}N^2H^{16}O^6 = C^{24}(C^8H^5O^4)NAdH^9,O^2. ?$$

ARPPE. *Ann. Pharm.* 96, 106.

*Phenyl-malamide.*

Formed together with malanil (p. 319) by fusing malic acid with aniline. The product treated several times with boiling water, is resolved into a nearly colourless solution containing malanil, and a strongly coloured residue consisting chiefly of malanilide, which may be obtained pure and colourless by crystallisation from boiling alcohol, with the aid of animal charcoal.

Colourless scales having a faint lustre. Melts, with partial decomposition, at 175°, and at a higher temperature volatilises for the most part unaltered. When set on fire, it burns with a bright smoky flame.

| | | | Arppe. |
|---|---|---|---|
| 32 C | 192 | 67·61 | 67·66 |
| 2 N | 28 | 9·86 | |
| 16 H | 16 | 5·63 | 5·70 |
| 6 O | 48 | 16·90 | |
| $C^{32}N^2H^{16}O^6$ | 284 | 100·00 | |

Malanilide is nearly insoluble in *water*, and in dilute *hydrochloric acid*, *ammonia* and *potash*. It dissolves but sparingly also in *alcohol* and *ether*. Strong *sulphuric acid* dissolves it with the aid of heat. *Nitric acid* dissolves it in the cold, forming a yellow solution.

When boiled with strong caustic *potash*, it dissolves and is for the most part decomposed, a fatty substance rising to the surface of the liquid. On addition of water, the dissolved semifluid portion is converted into a white insoluble powder, which may be completely freed from potash by washing with water. This powder dissolves with some difficulty in alcohol, and crystallises therefrom in small crystalline groups and needles. It may be heated, without visible alteration, to 225°; melts at a higher temperature, and if cautiously heated, yields a crystalline laminar sublimate and leaves a small quantity of charcoal. This substance gives by analysis 64·17 p. c. carbon and 5·41 hydrogen; hence it appears to be *tartanilide*, $C^{32}N^2H^{16}O^8 = 2C^{12}NH^7 + C^8H^6O^{12} - 4\ HO$. (Arppe.)

## ¶. Itaconanilide.

$$C^{34}N^2H^{16}O^4 = C^{24}(C^{10}H^5O^2)NAdH^9,O^2. ?$$

GOTTLIEB. *Ann. Pharm.* 77, 282.

*Phenyl-itaconamide.*

When itaconic acid is heated with excess of aniline to a temperature a little above 182°, water and excess of aniline distil over, and the residue on cooling solidifies for the most part in a crystalline mass consisting chiefly of itaconanilide, which may be purified by two or three crystallisations from boiling alcohol. It is also produced by the action of citraconic acid on aniline.

Large, light, delicate scales, having a nacreous lustre like that of the fatty acids. Melts at 185°, and solidifies in a crystalline mass on cooling. May be sublimed in small quantities without decomposition. Its vapour has a pungent odour.

| | | | Gottlieb (*mean*). |
|---|---|---|---|
| 34 C | 204 | 72·85 | 72·84 |
| 2 N | 28 | 10·00 | |
| 16 H | 16 | 5·72 | 5·84 |
| 4 O | 32 | 11·43 | |
| $C^{34}N^2H^{16}O^4$ | 280 | 100·00 | |

$$= 2C^{12}NH^7 + C^{10}H^6O^8 - 4HO.$$

Nearly insoluble in cold *water*, very sparingly soluble in boiling water; dissolves readily in *alcohol* and *ether*.

Aqueous acids and alkalis do not act upon it, even at the boiling point.

Strong *sulphuric acid* dissolves it, forming a brown solution from which it is precipitated without alteration by water.

## ¶. Pentanitro-itaconanilide.

$$C^{34}N^7H^{11}O^{24} = C^{24}(C^{10}H^5O^2)NAdX^5H^4,O^2.$$

GOTTLIEB. *Ann. Pharm.* 85, 38.

Itaconanilide dissolves in a mixture of strong nitric and sulphuric acids; and on adding water to the solution, a pale yellow pulverulent body is precipitated, which, after washing with water, gives up to boiling alcohol a very small quantity of a substance, which crystallises from the solution in small yellow scales, while the principal product of the reaction is a perfectly amorphous substance, which produces stains, is destitute of

taste and odour, and insoluble in water and alcohol. This is the nitro-compound.

| | Dried at 100°. | | | | Gottlieb. |
|---|---|---|---|---|---|
| 34 C | 204 | .... | 40·39 | ........ | 40·45 |
| 7 N | 7 | .... | 2·18 | ........ | 2·36 |
| 11 H | 11 | .... | 38·03 | ........ | 38·00 |
| 24 O | 112 | .... | 19·40 | ........ | 19·19 |
| $C^{34}N^2X^5H^{11}O^4$ | 334 | .... | 100·00 | ........ | 100·00 |

The compound when treated with alkalis, does not yield binitraniline. (Gottlieb.)

## ¶. Sulphophenanilide.

$$C^{24}NH^{11}S^2O^4 = C^{12}(NH,C^{12}H^5)H^5,S^2O^4.$$

Biffi. *Ann. Pharm.* 91, 107.

Chloride of sulphophenyl (p. 174) mixed with aniline becomes heated and forms an oily liquid, which crystallises from solution in alcohol in splendid prisms with pyramidal summits. Melts at 110°; sinks in boiling water, in the form of a heavy oil. Dissolves very sparingly in water, readily in alcohol and ether.

| | | | | | Biffi. |
|---|---|---|---|---|---|
| 24 C | 144 | ........ | 61·80 | ........ | 61.8 |
| N | 14 | ........ | 6·01 | ........ | 6·0 |
| 11 H | 11 | ........ | 4·73 | ........ | 5·0 |
| 2 S | 32 | ........ | 13·73 | | |
| 4 O | 32 | ........ | 13·73 | | |
| $C^{24}NH^{11}S^2O^4$ | 233 | ........ | 100·00 | | |

$$= \left.\begin{matrix} C^{12}H^5S^2O^4 \\ C^{12}H^5 \\ H \end{matrix}\right\} N,$$ = nitride of sulphophenyl, phenyl, and hydrogen. ¶.

### *Azo-nucleus* $C^{12}N^2H^4$.

## Diphanine.

$$C^{12}N^2H^6 = C^{12}N^2H^4,H^2.$$

Laurent & Gerhardt. (1849.) *Compt. chim.* 1849, 417; abstr. *Ann. Pharm.* 75, 74.

*Preparation.* Binitrazobenzene is boiled with alcohol and hydrosulphate of ammonia till the alcohol is partially expelled; after which the

liquid is diluted with water, supersaturated with hydrochloric acid, filtered hot, and the filtrate supersaturated with ammonia. The crystalline alkaloid thus precipitated is purified either by recrystallisation from ether, or by pouring dilute sulphuric acid over it, washing the sulphate of diphanine with cold water and alcohol, dissolving it in boiling water containing hydrochloric acid, and precipitating by ammonia.

*Properties.* Yellow, crystalline.

| | | | Laurent & Gerhardt. |
|---|---|---|---|
| 12 C | 72 | 67·92 | 67·0 |
| 2 N | 28 | 26·42 | |
| 6 H | 6 | 5·66 | 5·8 |
| $C^{12}N^2H^6$ | 106 | 100·00 | |

Laurent & Gerhardt double the formula, making it $C^{24}N^4H^{12}$.

It dissolves with a fine red colour in hydrochloric or nitric acid.

Its hydrochloric acid solution forms with bichloride of platinum a carmine-coloured precipitate, containing:

| | | | Laurent & Gerhardt. |
|---|---|---|---|
| 12 C | 72·0 | 23·06 | |
| 2 N | 28·0 | 8·97 | 9·4 |
| 7 H | 7·0 | 2·24 | |
| Pt | 99·0 | 31·71 | 30·5 |
| 3 Cl | 106·2 | 34·02 | |
| $C^{12}N^2H^6,HCl + PtCl^2$ | 312·2 | 100·00 | |

*Azo-nucleus* $C^{12}N^6$.

## Paracyanogen.

$C^{12}N^6$.

JOHNSTON. *N. Edinb. J. of Sc.* 1, 75; also *Schw.* 56, 341. *Ann Pharm.* 22, 280.
POLYD. BOULLAY. *J. Pharm.* 16, 180; also *Scher.* 60, 107; also *Br. Arch.* 34, 32; abstr. *Pogg.* 20, 63.
THAULOW, *J. pr. Chem.* 31, 220.
SPENCER. *J. pr. Chem.* 30, 478.
H. DELBRÜCK. *J. pr. Chem.* 41, 161.

*Solid Cyanogen, Bicarburet of Azote, Stickkohlenstoff.*

*Formation.* 1. When certain metallic cyanides are ignited in close vessels: *e. g.* cyanide of mercury (viii, 14); cyanide of silver (viii, 27); ferrocyanide of lead. (Thaulow.) When moist cyanide of mercury is heated, the residue contains more than 2C to 1N, because a proportionately larger quantity of

N than of C is consumed in the formation of carbonate of ammonia; in this case also the residue is difficult to free from mercury, contains a certain quantity of H and O, dissolves in great part in water when repeatedly washed, forming a light blue solution, and finally leaves a paracyanogen containing too much carbon. (Delbrück.) — 2. When azulmic acid is heated in close vessels.

*Preparation.* 1. When perfectly dry cyanide of mercury is heated in a retort, till all the mercury is volatilised together with the cyanogen gas, paracyanogen remains behind. (Johnston.) — When an iron tube welded at the bottom is filled with cyanide of mercury, closed at top by a screwed plug having a hole through it into which gypsum paste is poured, and heated to low redness, the vapour of mercury escapes but slowly through the gypsum as it becomes porous by the heat; and under the increased pressure thus produced, a larger quantity of cyanogen remains in the form of paracyanogen. (Brown, *Edinb. Phil. Trans.* 1, 245; *Berz. Jahresb.* 22, 289.) — 2. Ferrocyanide of lead (vii, 490) is ignited out of contact with the air; the cooled mass exhausted, first with warm dilute nitric acid, then with oil of vitriol; and the paracyanogen precipitated by water from its solution in the oil of vitriol. (Thaulow.) The paracyanogen is not actually dissolved in the oil of vitriol, or only to a scarcely perceptible amount, but merely suspended. If therefore the liquid be filtered through asbestus, a dark brown filtrate is obtained from which water throws down only a trace of paracyanogen, and on the asbestus in the funnel there remains a quantity of charcoal free from nitrogen. (Berzelius, *Jahresber.* 23, 84.) — 3. Azulmic acid precipitated by the decomposition of hydrocyanic acid or alcoholic cyanogen, is ignited out of contact with the air. (Johnston.)

*Properties.* The product obtained by (1) is a brown-black, loosely coherent, soft, tasteless, inodorous mass, which soils the fingers. (Johnston.) It was sometimes obtained by Johnston in the form of a greenish black, dense, hard, easily friable mass, which, when deposited in thin layers on a tube, appeared brown-red by transmitted light.

Paracyanogen (1) burnt with chlorate of potash, yields on the average 198 measures of carbonic acid gas to 100 of nitrogen, and therefore contains 1 At. N to 2 At. C, or a multiple. (Johnston.)

*Decompositions.* 1. When paracyanogen obtained from dry cyanide of mercury is strongly *ignited* in a closed vessel, or in a stream of dry nitrogen or carbonic acid gas, it is completely converted into cyanogen gas without leaving any residue. (Delbrück.) Paracyanogen obtained from moist cyanide of mercury, is likewise converted into gaseous cyanogen by ignition, but leaves a residue of charcoal. (Delbrück.) — 2. Paracyanogen (1) heated to redness in the air, burns slowly away without smoke, but with a comparatively greater diminution of carbon than of nitrogen, so that at first there remains a compound containing 6 C to 4 N, then a compound of about 6 C to 5 N, and lastly *Protocarburet of Azote,* which contains C and N in equal numbers of atoms [$= C^{12}N^{12}$ ?], and when ignited for a longer time, burns completely away, without any further relative diminution of the amount of carbon. When cyanide of mercury is ignited in contact with the air, the same protocarburet of azote remains, amounting to 2·33 per cent. (Johnston.) — 3. Dry *chlorine gas* passed over paracyanogen obtained from cyanide

of mercury, produces thick white fumes, having a suffocating odour and condensing in the form of a white body in the receiver. This substance may be sublimed without alteration; it is inodorous, permanent in the air, yields when fused with carbonate of soda, a mass which exhibits the reactions of cyanogen and chlorine, and dissolves in hot water, forming a solution which does not exhibit the reactions of cyanogen. (Delbrück.) Paracyanogen obtained from cyanide of silver, likewise forms with chlorine, copious white fumes, but no sublimate. The apparatus emits the mouse-like odour of fixed chloride of cyanogen, and the escaping gas has a pungent odour probably of volatile chloride of cyanogen. (Delbrück.) — 4. Paracyanogen ignited in a stream of hydrogen gas, is resolved into ammonia, hydrocyanic acid, and charcoal (Delbrück):

$$C^{12}N^6 + 12H = 3NH^3 + 3C^2NH + 6C.$$

or:

$$C^{12}N^6 + 10H = 2NH^3 + 4C^2NH + 4C.?$$

Nitric acid neither decomposes paracyanogen (1) nor dissolves it. (Johnston, Delbrück.) But, when paracyanogen obtained from cyanide of silver is evaporated to dryness with nitric acid, and the residue slightly heated, it assumes a light yellow colour, dissolves in nitric acid and may be precipitated therefrom by water. (Delbrück.) — Paracyanogen mixed with chlorate of potash detonates by heat, but not by percussion. (Johnston.) Sulphur does not act upon paracyanogen, either when the two are heated together, or when the vapour of the sulphur is passed over heated paracyanogen. (Delbrück.) — Respecting Brown's alleged conversion of paracyanogen into silicium, compare Smith & Brett (*Phil. Mag. J.* 19, 295 ; 20, 1).

*Combinations.* Paracyanogen (1) is insoluble in water. (Delbrück.)

It dissolves in warm *oil of vitriol.* (Compare however Berzelius, p. 372.)— The solution yields on evaporation a greyish black residue insoluble in water; it appears to be capable of forming a crystalline compound with mercury. (Johnston.)

It dissolves in hot concentrated *hydrochloric acid*, forming a light yellow solution, which, when evaporated, leaves an abundant residue insoluble in water. (Johnston.)

It does not dissolve in nitric acid or in ammonia. (Johnston.)

It dissolves in aqueous potash, but probably undergoes decomposition at the same time. (Johnston.)

*Paracyanide of Silver.* — Remains when cyanide of silver is ignited in close vessels (viii, 27), as a grey, porous, very refractory mass, which, when struck with the hammer, acquires a perfect metallic lustre like that of bismuth, and becomes hard and brittle, so that it may be crushed to a fine powder. (Thaulow.) Greyish silver-white, hard and brittle (Delbrück.)

Paracyanide of silver very strongly ignited in a retort yields nitrogen and cyanogen gases, at first in the proportion of 1 vol. nitrogen gas to 1·5 vol. cyanogen; then of 1 : 2·4; then of 1 : 0·86; and lastly of 1 : 0·9. — 134 pts. (1 At.) of cyanide of silver strongly ignited in a retort, till the paracyanide of silver formed at first, is decomposed, gives off 20·44 pts. in the form of nitrogen and cyanogen gases (1·34 grm. of cyanide of silver yielding 94 cubic centimetres of the gaseous mixture.)

The residue, which has exactly the appearance of silver, leaves, when boiled with nitric acid, 5·8 pts. of nitrogenous charcoal, which when burnt yields 1 vol. nitrogen to 3·5 vol. carbonic acid gas, therefore 3·5 pts. carbon to 2·3 pts. nitrogen. The 26 pts. of cyanogen in 134 pts. of cyanide of silver are therefore resolved into 20·44 pts. of gaseous mixture and 5·8 pts. of nitrogenised charcoal; 20·44 + 5·8 = 26·24; and the silver retains a proportionally larger quantity of carbon than of nitrogen, so that the cyanogen gas evolved is mixed with free nitrogen. (Delbrück.) — Nitric acid digested with paracyanide of silver, extracts the greater part of the silver and leaves a brown residue. (Thaulow.) The residue left after the paracyanide of silver has been repeatedly boiled with fresh nitric acid, contains, in the dried state, together with carbon and nitrogen in the proportion of 2 At. to 1 At., also 43·4 p. c. silver, which remains after ignition in contact with the air. It therefore contains $AgC^6N^3$ [or rather, $Ag^2C^{12}N^6$]. (Liebig, *Ann. Pharm.* 50, 357). Paracyanide of silver [the residue after treatment with nitric acid appears to be meant] yields, when heated to bright redness, a mixture of nitrogen and cyanogen gases in proportions varying in the course of the experiment as follows: 1 : 8; 1 : 5; 1 : 4; and finally 1 : 8 again; hence charcoal remains together with the silver. (Liebig.) Paracyanide of silver cannot be completely freed from silver by boiling with nitric acid; the silver may however be entirely removed by treating the brown friable residue obtained by the action of nitric acid, with mercury, or by dissolving it in oil of vitriol and precipitating by water. (Delbrück.) The brown pulverulent residue obtained by treating paracyanide of silver with moderately strong nitric acid, gives off, when dried over oil of vitriol and ignited in the air, a faint odour of hydrocyanic acid, and leaves 40·24 p. c silver, which dissolves in nitric acid all but a mere trace. It dissolves in slightly heated oil of vitriol, without evolution of gas, and water added to the dark brown solution throws down brown flakes, which, after drying at 175°, leave 35·46 p. c. silver when ignited in the air. — These brown flakes, twice boiled with nitric acid, and then washed and dried, leave by ignition 32·8 p. c. silver. It appears then that the silver is not completely extracted, either by nitric acid or by oil of vitriol. (Rammelsberg, *Pogg.* 73, 84.)

Paracyanide of silver unites with mercury, forming an extremely hard crystalline amalgam. This amalgam once digested with nitric acid, leaves a residue which, when pulverised, dissolves completely in excess of oil of vitriol even without the aid of heat. Water added to this solution throws down paracyanogen, while the silver remains dissolved in the dilute acid. If the residue is not pulverised, it does not dissolve in oil of vitriol unless heat be applied, and then gives off a gas, which is not sulphurous acid. (Thaulow.) — Paracyanide of silver surrounded with magnesia, and exposed, in a hessian crucible, to the most intense heat of a Sefström's blast furnace, yields metallic globules of silver containing magnesium, and soluble without colour in nitric acid. — By tolerably strong ignition, for half an hour in a crucible lined with charcoal, paracyanide of silver does not undergo any change in form or appearance, but nevertheless exhibits a few granules of reduced silver. (Thaulow.) It is not altered by ignition with cyanide of potassium. (Thaulow.)

Paracyanogen is insoluble in alcohol. (Johnston.)

¶. When hydrocyanic acid is added to a mixture of potash and ferricyanide of potassium, the solution acquires a yellow colour, soon changing however to dark red

and even black, and yields a precipitate of the same colour, the formation of which is accelerated by heat. This compound is insoluble in water, but soluble in caustic alkalis, and reprecipitated by acids; it gives off 10·5 p. c. water at 100°. It contains carbon and nitrogen, but not in the proportions to form paracyanogen, the carbon being in excess, and likewise oxygen and hydrogen. Different specimens gave results varying from 48·92 to 42·05 p. c. C; 41·62 to 42·77 N; and 3·2 to 3·4 H. A similar substance is formed by passing chlorine through a solution of cyanide of potassium: the product thus obtained gives 35·2 to 36·2 C; 42·30 N; and 3·00 H. When treated with nitric acid, it forms a yellow compound (Lyon Playfair, *Chem. Soc. Q. J.* viii, 129). ¶.

*Appendix to Paracyanogen.*

## Azulmic Acid.

Johnston. *Schw.* 56, 341.
Pol. Boullay. *J. Pharm.* 16, 180; also *Schw.* 60, 107.
H. Delbrück. *J. pr. Chem.* 41, 161.

*Stickkohlenstoff, Azulmsäure, Azulmin, Acide azulmique* (Boullay), *Azulmine* (Thénard).

First noticed and examined in some of its relations by Proust in 1806 (*Ann. Chim.* 60, 233; also *N. Gehl.* 3, 584), then by Ittner in 1809 (*Beiträge z. Geschichte d. Blausäure*), and by Gay-Lussac in 1811; afterwards somewhat more minutely by Johnson and Boullay; frequently confounded with paracyanogen, from which however it differs by containing hydrogen.

*Formation.* In many decompositions of cyanogen and hydrocyanic acid. (vii, 386, 6; 387, 7; 402, 12.)

*Preparation.* An aqueous or a dilute alcoholic solution of cyanogen or aqueous hydrocyanic acid is left to itself for some time — best after addition of a small quantity of ammonia or of potash — as long as the liquid, which gradually acquires a brown colour, continues to deposit brown flakes; and these flakes are collected on a filter and washed with water. The water takes up a portion of them, becoming brown thereby, the solution being caused by the ammonia produced in the decomposition or perhaps by the ammonia or potash added. This portion may be precipitated by an acid.

*Special modes of preparation:* 1. Concentrated — or better, anhydrous — hydrocyanic acid is left to itself till it solidifies in a brown mass, which is washed with water and dried.

2. Hydrated alcohol saturated with cyanogen gas is left to stand as long as flakes are deposited in it; and these flakes are collected on a filter, the alcohol then running off colourless, afterwards washed with water, which then becomes yellow, and dried. (Johnston.)

3. An aqueous solution of cyanogen is abandoned to spontaneous decomposition, and the brown precipitate washed with water, and dried. (Pelouze & Richardson, *Ann. Pharm.* 26, 63.)

4. Alcoholic potash is saturated with cyanogen gas; the liquid decanted from precipitated cyanide of potassium; set aside for some time

in a bottle, which is closed with the stopper of a dropping bottle having a narrow tube passing through it; and after four months, when the odour of hydrocyanic acid is no longer perceptible, slowly evaporated to dryness. The residue is then macerated in cold water, thrown on a filter and washed with water, to which it imparts a yellow colour. The azulmic acid thus obtained leaves a small quantity of carbonate of potash, when burnt, but may be obtained pure by solution in oil of vitriol, precipitation by rather more than an equal volume of water, and subsequent washing and drying. (Thaulow, *J. pr. Chem.* 31, 228.)

5. Hydrocyanic acid may also be mixed with small quantities of ammonia or potash (Gm.), or its vapours passed into aqueous cyanide of potassium, or the aqueous cyanide of potassium mixed with a quantity of sulphuric acid not sufficient to decompose it (Delbrück); in either case an abundant deposit is quickly obtained. The product obtained with hydrocyanic acid and cyanide of potassium is however a mixture of three substances, of which one is soluble in water, another in acids, while a body richer in carbon remains behind. (Delbrück.)

6. Cyanide of potassium prepared by the method given at page 413, 5, vol. vii, is dissolved in cold water; chlorine gas passed through the solution, of sp. gr. 1·2, till it begins to effervesce, becoming heated at the same time to 85°, and giving out white fumes; the liquid set aside for some hours, whereupon it becomes turbid, acquires a dark colour, and deposits black flakes; and the red liquid decanted from these flakes (it may yield more if treated with fresh chlorine), which are then washed with a small quantity of ice-cold water, in which they appear to be somewhat soluble, and dried. Bromine or iodine may also be used instead of chlorine. (Spencer, *J. pr. Chem.* 30, 478.) The product thus obtained is a mixture of two substances, one of which dissolves with brown colour in water, and the other for the most part in boiling nitric acid. (Delbrück.) In general, azulmic acid exhibits different properties according to the mode in which it is prepared. (Delbrück.)

*Properties.* Azulmic acid (1) is a black spongy mass, yielding a brown powder, which, in fine particles, transmits light with red brown colour (Boullay); (2) is black in the mass, brown when pulverised (Johnston); (3) black (Pelouze & Richardson).

With regard to the *composition* of azulmic acid, statements vary to such an extent as to render it impossible to calculate a formula. As Delbrück has shown that many preparations bearing the name of azulmic acid, are mixtures of three substances, one of which is soluble in water, another in nitric acid, and the third insoluble in both liquids, it is doubtful whether a pure compound has ever been analysed. The following are the individual statements :

Azulmic acid (1), purified by solution in potash, precipitation by acids, washing, and drying, yields by combustion 5 vol. carbonic acid gas to 2 vol. nitrogen, and appears to be $= C^5N^2H$. (Boullay). — The acid (2) contains 26 pts. (1 At.) cyanogen to 4·05 (4 At.) hydrogen, and is therefore $= C^2NH^4$ (Johnston, *Schw.* 56, 346.) Acid (1) and acid (2) are $C^3N^2H,2HO$ [$= C^6N^4H^6O^4$] (Johnston, *Ann. Pharm.* 22, 280). Acid (4) yields by combustion 2 vol. carbonic acid gas to 1 vol. nitrogen. (Thaulow.) — Acid (3) in combination with oxide of silver exhibits the composition $C^8N^4H^4O^4$ (Pelouze & Richardson). — Acid (4) contains about 4 At. C to 1 At. N; but it is a mixture (*vid. sup.*), so that the proportion varies in different preparations. (Delbrück.)

*Decompositions* 1. Azulmic acid (1) yields by dry distillation, hydrocyanic acid, ammonia, and water, and leaves charcoal containing nitrogen. (Proust). It yields a sublimate of hydrocyanate of ammonia, and when more strongly heated, a gas smelling of cyanogen, but burning with a blue flame, and leaves charcoal. (Boullay.) The acid (1) or (2) which is $C^6N^4H^4O^4$, gives off, when ignited, carbonate of ammonia together with a small quantity of water, and leaves paracyanogen. $C^6N^4H^6O^4 = 2(NH^3,CO^2) + C^4N^2$. (Johnston.) — Acid (4) when gently heated, gives off a large quantity of hydrocyanic acid and hydrocyanate of ammonia, and leaves a residue which contains more carbon than cyanogen contains, and is therefore resolved by strong ignition into cyanogen gas and charcoal free from nitrogen. — 2. Chlorine gas passed over azulmic acid, gives off white fumes having a pungent odour and perhaps containing volatile chloride of cyanogen; no sublimate is formed, but the apparatus exhibits the mouse-like odour of solid chloride of cyanogen. (Delbrück.) The acid (1) dissolves in cold concentrated nitric acid. The aurora-red solution is precipitated by water; when evaporated, it leaves a pitchy residue, sparingly soluble in cold, better in hot water, and easily soluble in potash-ley, from which acids throw down a body resembling indigo-resin. (Boullay.) The acid (1) dissolves readily in nitric acid, and water added to the yellow solution throws down *paracyanic acid* in the form of a yellow powder. (Johnston.)

*Paracyanic acid* $= C^8N^4O$; when subjected to dry distillation, it gives off carbonic acid and cyanogen gases, and leaves paracyanogen. *Mercuric paracyanate* is precipitated even from the hot solution of paracyanic acid in nitric acid [on addition of mercuric nitrate?]; it is $= 2HgO,C^8N^4O$. *Paracyanate of silver* is $AgO,C^8N^4O$. (Johnston.)

The solution of azulmic acid (1) in nitric acid is but partially precipitated by water; ammonia throws down the whole of the dissolved matter in thick brown flakes. Lead and silver salts precipitate the nitric acid solution more completely than water; but the liquid filtered from the silver precipitate still forms with ammonia a thick brown precipitate containing 3·07 per cent. of oxide of silver. The nitric acid solution of azulmic acid neutralised with ammonia as far as possible without precipitation, forms with neutral acetate of lead, a thick white precipitate; with copper-salts a light green; and with manganese-salts, after addition of sal-ammoniac and ammonia, a light brown precipitate. When the nitric acid solution of azulmic acid is precipitated by nitrate of silver without addition of ammonia, the precipitate contains 31·98 p. c. oxide of silver; if ammonia be added immediately, but not in sufficient quantity to produce alkaline reaction, the precipitate contains 19·35 p. c. oxide of silver. These numbers do not agree with Johnston's formula, which requires 51 p. c. oxide of silver. (Delbrück.)

4. Azulmic acid ignited with carbonate of potash forms cyanide of potassium. (Ittner.)

*Combinations.* Washed azulmic acid (1) is insoluble in *water* (Boullay); (3) dissolves sparingly. (Pelouze & Richardson.)

The acid (4) dissolves in *oil of vitriol* whence it is precipitated by water. (Thaulow.)

It dissolves in concentrated *hydrochloric acid.* (Thaulow.)

The acid (1) dissolves easily in aqueous *ammonia* or *potash* forming a dark brown-red solution; acids throw down from this solution a red-brown powder; heavy metallic salts decolorise it and form brown

precipitates. The acid (4) is likewise soluble in carbonate of potash. (Thaulow.)

Alcohol recently saturated with cyanogen gas does not precipitate *corrosive sublimate;* but after the solution has turned brown, it forms therewith, a brown precipitate afterwards turning red, which yields by combustion, 2 vol. carbonic acid gas to 1 vol. nitrogen. — *Nitrate of silver* forms a black precipitate with alcohol saturated with cyanogen gas, after the solution has turned brown. (Johnston.)

Azulmic acid (3) dissolves readily in *acetic acid.* (Pelouze & Richardson.)

Azulmic acid (1), (2), and (4), is insoluble in alcohol (Boullay, Johnston, Thaulow); (3) is sparingly soluble in alcohol, insoluble in ether. (Pelouze & Richardson.)

Boullay likewise regards the mouldy substance which remains when cast iron is dissolved in nitric acid, (v, 216) as azulmic acid. — Boullay also obtained a similar substance by boiling gelatin with potash. (vid. *Gelatin.*)

Girardin & Preisser (*N. Ann. Chim. Phys.* 9, 377) boiled the substance of corpses which had mouldered in leaden coffins in a church, with potash-ley, and, by precipitating with acids, and washing the precipitate with ether, alcohol, and water, obtained a red-brown, light crystalline powder, amounting to 35·5 per cent. of the original mass; this powder was resolved by dry distillation into hydrocyanate of ammonia and charcoal, and contained 50·23 per cent. C, 47·90 N and 1·68 H (loss 0·19) so that it was = $C^5N^2H$, therefore = Boullay's azulmic acid.

## *Primary nucleus* $C^{12}H^8$.

### Oil. $C^{12}H^8$.

FARADAY. (1825.) *Phil. Trans.* 1825, 140; also *Schw.* 47, 340 and 441; also *Pogg.* 5, 303.

COUERBE. *Ann. Chim. Phys.* 69, 184; also *J. pr. Chem.* 18, 165.

*Hexacarbure quadrihydrique* (Couerbe).

*Formation.* By the dry distillation of fats and resins.

*Preparation.* In the preparation of butylene (x, 66); a certain portion of benzene however remains dissolved even after strong cooling. (Faraday.) The resin-oil (x, 411), which, when distilled gives off at first an oil resembling amylene (xi, 2), then likene (x, 411), and the oil $C^{12}H^{10}$ (xi, 411), yields at a higher temperature, the oil $C^{12}H^8$. (Couerbe.)

*Properties.* Colourless oil, of sp. gr. 0·86 at 15·5°, boiling at 85·5°, and having a vapour-density of about 3·049. (Faraday.) Very pale yellow; of sp. gr. 0·8022; boiling between 80° and 85°; vapour-density 2·802. (Couerbe.)

| | | | Faraday. | Couerbe. |
|---|---|---|---|---|
| 12 C | 72 | 90 | 89·58 | 89·79 |
| 8 H | 8 | 10 | 10·42 | 9·77 |
| $C^{12}H^8$ | 80 | 100 | 100·00 | 99·56 |

| | Vol. | Density. |
|---|---|---|
| C-vapour | 12 | 4·9920 |
| H-gas | 8 | 0·5546 |
| Oil-vapour | 2 | 5·5466 |
| | 1 | 2·7733 |

*Decompositions.* 1. The oil burns with a bright flame which deposits a large quantity of soot. — 2. In contact with oil of vitriol, it acquires a dark colour, becomes strongly heated, and is resolved into a lower thick black layer containing a conjugated sulphuric acid, and an upper thin yellow liquid, which is not further altered by cold oil of vitriol. — Potassium has no action upon it at 85·5°. (Faraday.)

*Combinations.* The oil dissolves very sparingly in *water,* very readily in *alcohol* (whence it may be separated by water) in *ether* and in *oils* both *fixed* and *volatile.* (Faraday.)

*Oxygen-nucleus* $C^{12}H^6O^2$.

## Pyrocatechin.

$C^{12}H^6O^4 = C^{12}H^6O^2,O^2$.

REINSCH. *Repert.* 68, 54.
WACKENRODER. *Ann. Pharm.* 37, 309.
CONST. ZWENGER. *Ann. Pharm.* 37, 327.
RUDOLF. WAGNER. *J. pr. Chem.* 52, 450; 55, 65.
EISSFELDT. *Ann. Pharm.* 92, 101.
MAX. BUCHNER. *Ann. Pharm.* 96, 186.

*Pyromoritannic acid, Phenic* or *Oxyphenic acid.* — First obtained by Reinsch in 1839; more exactly investigated by Zwenger, Wagner, Eissfeldt and Buchner.

*Formation.* By the dry distillation of catechin (Reinsch, Zwenger), of moritannic acid, gum ammoniacum and probably also of peucedanin (Wagner), of kino (Eissfeldt); also of wood, whence it is found in wood-vinegar. (Buchner.) — It does not occur in coal-tar. (Buchner.)

*Preparation.* 1. Catechin or catechu is introduced into a retort of fourfold capacity, and quickly heated above its melting point until it chars; the distillate which collects in the cooled receiver, evaporated at 30° till crystals form on the surface, the empyreumatic oils which become

resinised during the evaporation being separated by filtration; the black-brown crystalline mass which forms on cooling, sublimed (after pressure between paper, according to Wagner), a large quantity of liquid then passing over at first, which also yields pyrocatechin by evaporation; and the sublimation of the crystals repeated three or four times, till they no longer become coloured on exposure to the air. (Zwenger.) — 2. Crude moritannic acid mixed with an equal quantity of quartz-sand is heated in a retort over a moderate fire; and the distillate, which solidifies on cooling, freed from the oil containing carbolic acid by pressure between paper, and purified by sublimation and recrystallisation from water. (Wagner.) — ¶. 3. Malabar kino or butea-kino yields by dry distillation a clear watery liquid smelling of creosote, and leaving, after separation from empyreumatic oil, and evaporation, a black crystalline mass, which when sublimed, yields pyrocatechin in thin colourless laminæ, and sometimes in rhombic prisms. From malabar kino (but not from butea-kino), a small quantity of pyrocatechin may also be obtained by extraction with ether and evaporation, — or by precipitating the aqueous extract with acetate of lead, decomposing the lead precipitate with sulphuretted hydrogen, evaporating, and digesting the residue in ether. (Eissfeldt.) — 4. Crude wood-vinegar evaporated to a syrup is shaken up with a saturated solution of common salt; the liquid separated from the tarry matter and agitated with ether; the ethereal liquid separated from the saline solution and the ether distilled off; and the residue (containing pyrocatechin, acetic acid and tar-oil) distilled in a stream of carbonic acid, whereupon acetic acid passes over first, then pyrocatechin and tar-oil, then a brown viscid oil. The middle portion of the distillate, which must be collected apart, solidifies on cooling in a reddish yellow crystalline pulp, which, when pressed between bibulous paper and sublimed in a stream of carbonic acid, yields colourless pyrocatechin. Or better: The wood-vinegar is shaken up with ether without previous evaporation; the residue obtained from the ethereal liquid by distilling off the ether, shaken up with a saturated solution of common salt; the saline solution, after separation from the oil, again shaken up with ether; the ether distilled off; and the residue also subjected to distillation; a liquid is then obtained, which, on cooling, yields tolerably pure crystals of pyrocatechin. (Buchner.) ¶.

*Properties.* — Broad, white, strongly shining laminæ resembling benzoic acid, and rhombic prisms. (Zwenger.) Small shining rectangular prisms belonging to the right prismatic system; bevelled with two faces resting on the acute lateral edges at an angle of 116°. (Wagner & Neumann.) Melts at 116°*, and sublimes even at a lower temperature. (Zwenger.) Melts, after drying, between 110° and 115°, and volatilises gradually at 130° (between 50° and 60° according to Wagner); melts at 111° or 112°; when perfectly dry, and volatilises even at ordinary temperatures. (Eissfeldt.) Melts at 111°, and volatilises at the melting point, subliming in shining laminæ. (Buchner.) Boils between 240° and 245° (between 240° and 250°, according to Wagner), and yields colourless vapours which condense into a quickly crystallising oil. (Wagner.) The vapours have a pungent odour and excite coughing. Its taste is sharply bitter and burning, It is neutral. (Zwenger.) Rather bitter; scarcely

* In Zwenger's paper the melting point is stated to be 126°; but this is stated by Zwenger himself to be a misprint (vid. *Ann. Pharm.* 92, 108).

reddens litmus. Mixed with hydrochloric acid, it colours firwood violet, the colouring being stronger as the pyrocatechin is more free from carbolic acid. (Wagner.)

| | | | Zwenger, sublimed. | Zwenger, fused. | Wagner, dried at 80° then sublimed. |
|---|---|---|---|---|---|
| 12 C | 72 | 65·45 | 65·55 | 66·32 | 65·51 |
| 6 H | 6 | 5·46 | 5·60 | 5·62 | 5·86 |
| 4 O | 32 | 29·09 | 28·85 | 28·06 | 28·63 |
| $C^{12}H^6O^4$ | 110 | 100·00 | 100·00 | 100·00 | 100·00 |

| | Eissfeldt, fused. | Eissfeldt, dried. | Buchner, fused. | Buchner, sublimed and fused. |
|---|---|---|---|---|
| C | 65·06 | 64·91 | 68·62 | 68·39 |
| H | 5·86 | 5·52 | 5·91 | 5·96 |
| O | 29·08 | 29·57 | 25·47 | 25·65 |
| | 100·00 | 100·00 | 100·00 | 100·00 |

Eissfeldt's first analysis was made with pyrocatechin prepared from malabar-kino; the second from butea-kino. — Buchner explains the excess of carbon and hydrogen, on the supposition that the pyrocatechin had a small quantity of a hydrocarbon adhering to it.

Pyrocatechin is metameric with hydrochinone.

*Decompositions.* 1. Pyrocatechin turns yellow when heated, and becomes, as appears from the preceding analyses, somewhat richer in carbon. It also leaves a slight black residue when sublimed. This residue boiled with water, leaves an empyreumatic resin, and yields a brown decoction; on evaporating this liquid, a black film forms on the surface and a brown black residue is left.—From this residue, alcohol extracts a yellowish, translucent, amorphous substance (similar to Runge's viridic acid) whose aqueous solution acquires a green colour, gradually on exposure to the air, but immediately on addition of potash. The same solution forms with baryta-water a green precipitate; with neutral acetate of lead, a white precipitate which afterwards turns green; with ferrous salts a black; and with nitrate of silver a brown precipitate. (Zwenger.) Pyrocatechin may be distilled undecomposed even with excess of baryta or lime. (Wagner.) — 2. It burns with a bright flame. (Zwenger.) — 3. Its aqueous solution turns reddish in contact with the air, and may be evaporated without decomposition. (Zwenger.) — 4. It is rapidly decomposed by chlorate of potash and hydrochloric acid, yielding chloranil. (Wagner.) — 5. Nitric acid acts upon it with violence, evolving red vapours. (Zwenger.) The products of this reaction are oxalic acid and traces of a yellow nitro-acid, probably styphnic acid. (Wagner.) — 6. With aqueous chloride of lime or bichromate of potash, it forms a black liquid and a black precipitate. — 7. With aqueous caustic alkalis or alkaline carbonates it forms a mixture which is yellow at first, then becomes greenish yellow, and lastly black. (Zwenger.) The change of colour, accompanied by rapid absorption of oxygen, proceeds in the following order: green-brown, then black and opaque; with milk of lime: green, then quickly brown. (Wagner.) — The aqueous solution of pyrocatechin produces a greenish precipitate with silver solution, the silver being partly reduced, and a dark brown precipitate with solution of gold. To bichloride of platinum it gradually imparts a green colour and then forms a

greenish brown precipitate. (Zwenger.) It easily reduces nitrate of silver, terchloride of gold and bichloride of platinum; and at a boiling heat, sulphate or acetate of copper mixed with potash; it also imparts a brown colour to acetate of copper, and then forms a black-brown precipitate. (Wagner.) — It is not altered by sulphurous acid. (Wagner.) Buchner's oxyphenic acid exhibits similar reactions.

*Combinations.* Pyrocatechin dissolves readily in *water* (Zwenger, Wagner); also in *oil of vitriol* and hydrochloric acid. (Zwenger.)

It quickly absorbs *ammoniacal gas,* and gives it off again in vacuo or at 100°. (Zwenger.)

Its aqueous solution forms, with *neutral acetate of lead,* a thick white precipitate (yellowish white, according to Buchner), which is permanent in the air, nearly insoluble in water, but dissolves very readily in acetic acid. (Zwenger.) When dried in the cold, it appears greenish white, but brownish when dried at 100°. (Wagner.)

| | | | Zwenger, *at* 100°. | Eissfeldt, *at* 100°. | Buchner, *at* 100°. | *at* 115°. | Wagner. |
|---|---|---|---|---|---|---|---|
| 12 C | 72 | 22·78 | 23·25 | 22·80 | 22·41 | 22·13 | |
| 4 H | 4 | 1·27 | 1·35 | 1·34 | 1·53 | 1·39 | |
| 2 PbO | 224 | 70·89 | 70·01 | 70·43 | 70·08 | 71·76 | 69·47 |
| 2 O | 16 | 5·06 | 5·39 | 5·43 | 5·98 | 4·72 | |
| $C^{12}H^4Pb^2O^2,O^2$ | 316 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 | |

The aqueous solution of pyrocatechin does not colour ferrous salts (Wagner, Buchner); it colours ferric salts dark green and then forms a black precipitate (Zwenger); the dark green colour is changed by alkalis, even in very dilute solutions, to a beautiful violet-red, like that of permanganate of potash, and the green colour is restored by acids. (Wagner, Buchner.)

Pyrocatechin dissolves very readily in *alcohol* (Zwenger, Wagner), and very readily according to Zwenger, but with difficulty according to Buchner, in *ether.*

It does not precipitate gelatin (Zwenger, Wagner), or the salts of quinine. (Wagner.)

### *Oxygen-nucleus* $C^{12}H^4O^4$.

## Comenic Acid.

$$C^{12}H^4O^{10} = C^{12}H^4O^4,O^6.$$

ROBIQUET. *Ann. Chim. Phys.* 51, 326; also *J. Pharm.* 19, 67; also *Ann. Pharm.* 5, 90; also *Schw.* 67, 382.—*Ann. Chim. Phys.* 53, 428.

LIEBIG. *Ann. Pharm.* 7, 237; also *Pogg.* 31, 168.—*Ann. Pharm.* 26, 116.

STENHOUSE. *Phil. Mag. J.* 25, 196; also *Ann. Pharm.* 51, 237.

HENRY HOW. *Ed. Phil. Trans* xx, 2, 225; *Ann. Pharm.* 80, 65; abstr. *Chem. Soc. Qu. J.* 4, 363.

*Parameconic acid, Anhydrous meconic acid.* — Discovered, in 1832, by Robiquet, who at first regarded it as anhydrous meconic acid; afterwards recognized as a distinct acid by Liebig, who first observed the formation of carbonic acid which accompanies the conversion of meconic into comenic acid.

*Formation.* 1. By heating meconic acid to temperatures between 120° and 220°, the change being attended with evolution of carbonic acid :

$$C^{14}H^4O^{14} = C^{12}H^4O^{10} + 2CO^2.$$

2. By continued boiling of meconic acid dissolved in water or in hydrochloric acid, likewise with evolution of carbonic acid. (Robiquet.)

*Preparation.* Meconic acid (Liebig), or meconate of potash or baryta (Robiquet), is boiled with a strong mineral acid; or meconate of lime is boiled with highly concentrated hydrochloric acid (Stenhouse); or acid meconate of potash, produced by treating crude neutral meconate of lime with very dilute hydrochloric acid, is heated with as much strong hydrochloric acid as is required to dissolve it (How), and the solution left to crystallise. When the mere aqueous solution of the acid is boiled, too large a quantity of brown secondary product is formed. (Robiquet, Liebig.)

*Purification.* The still reddish crystals are dissolved in a slight excess of hot concentrated potash; the solution filtered hot to separate a small quantity of lime; the white nodules which form on cooling, washed with a small quantity of cold water, till the strongly coloured mother-liquor is removed; then boiled with excess of hydrochloric acid; and the comenic acid which separates on cooling, freed from hydrochloric acid by two or three recrystallisations from water. The still remaining tinge of red may be removed by treatment with animal charcoal. (Stenhouse.) — 2. The impure acid is dissolved in a quantity of boiling ammonia just sufficient to dissolve it (because an excess, as well as continued boiling, causes the liquid to turn brown), and filtered immediately at a boiling heat; the yellow crystals which separate from the dark filtrate when left at rest, washed with cold water, and recrystallised from hot water; their pale yellow aqueous solution mixed with strong hydrochloric acid; and the comenic acid, which is precipitated in the form of a white or pale yellow powder, crystallised from boiling water.

☞ *Properties.* Hard, yellowish, very acid, granular crystals. (Robiquet.) Prisms, laminæ, or granules, having a very faint yellowish colour. (How.)

The crystals are anhydrous. (Liebig.)

| *Crystals.* | | | Robiquet. | Liebig. |
|---|---|---|---|---|
| 12 C | 72 | 46·15 | 45·28 | 46·41 |
| 4 H | 4 | 2·57 | 3·65 | 2·69 |
| 10 O | 80 | 51·28 | 51·07 | 50·90 |
| $C^{12}H^4O^{10}$ | 156 | 100·00 | 100·00 | 100·00 |

*Decompositions.* 1. The acid, when subjected to dry distillation, behaves like meconic acid. (Robiquet.) When comenic (or meconic)

acid is quickly heated in a retort, above the temperature of 200° to 220°, at which pyromeconic acid would be formed, but not till complete carbonisation takes place, an acid, yellowish, watery liquid passes over having a faint empyreumatic odour; and there remains a blackish grey, porous, carbonaceous mass, from whose ammoniacal solution, after filtration, hydrochloric acid throws down thick dark green flakes, which, if exposed to the air after washing with water, shrink up to a substance resembling *glance-coal* in appearance, and in its chemical relations agreeing perfectly with metagallic acid. (Winckler, *Repert.* 59, 42.) — 2. Comenic acid suspended in water through which a stream of chlorine gas is passed, forms a solution of chlorocomenic acid which crystallises out after a while, and oxalic acid which remains in solution :

$$C^{12}H^{4}O^{10} + 2Cl = C^{12}ClH^{3}O^{10} + HCl.$$

The oxalic acid and a brown colouring matter which forms during evaporation, must be regarded as secondary products. (How.) — 3. Similarly, the colourless solution of comenic acid in bromine-water yields bromocomenic acid which crystallises, and oxalic acid. (How.) — 4. Nitric acid, even when very dilute, converts comenic acid into carbonic, hydrocyanic and oxalic acid, and if the nitric acid is tolerably strong and heated at the beginning of the action, the process is complete in a few minutes. (How.) — 5. Oil of vitriol acts upon comenic acid in the same manner as on meconic acid. (Robiquet.) — 6. The acid dissolved in water and boiled with excess of ammonia till nearly all the ammonia evaporates, forms a black-red liquid, which, on cooling, deposits impure comenamate of ammonia as a grey viscid sediment. (How) :

$$C^{12}H^{5}O^{10} + 2NH^{3} = C^{12}N^{2}H^{8}O^{8} + 2HO.$$

*Combinations.* The acid requires more than 16 pts. of boiling *water* to dissolve it. (Robiquet.)

The *Comenates* are partly *neutral* or *bibasic*, partly *acid* or *monobasic*. The neutral comenates of potash, soda and ammonia, cannot be obtained in the solid state. (How.)

*Comenate of Ammonia.* — *Monobasic.* — Obtained in How's process for purifying comenic acid. — The aqueous acid slightly supersaturated with ammonia, and evaporated in vacuo over oil of vitriol, yields four-sided prisms having a yellowish tinge; they give off 9·04 p. c. (2 At.) water at 100°. (Stenhouse.) White square prisms having a very strong lustre. They redden litmus even when they separate on cooling from a hot solution of the acid in excess of ammonia. They do not give off anything at 177°, but at 199° in a sealed tube, they melt and are converted into a black mixture of charcoal and comenamate of ammonia; their aqueous solution is also converted into this salt by continued boiling with ammonia (p. 393). They dissolve readily in boiling water, sparingly in alcohol. (How.)

| *Crystals dried at* 100°. | | | Stenhouse. |
|---|---|---|---|
| 12 C | 72 | 41·62 | 41·91 |
| N | 14 | 8·09 | 8·04 |
| 7 H | 7 | 4·05 | 4·14 |
| 10 O | 80 | 46·24 | 45·91 |
| $C^{12}H^{3}(NH^{4})O^{10}$ | 173 | 100·00 | 100·00 |

The same composition was found by How; if, however, the acid be neutralised with ammonia and mixed with alcohol, radiating prisms separate which give off 13·73 p. c. water at 100°, and are therefore $C^{12}H^3(NH^4)O^{10} + 3Aq$. (How.)

*Comenate of Potash.* — *a. Bibasic.* — The aqueous acid half neutralised with potash [so as to form the monobasic salt] yields no precipitate, but when completely neutralised, deposits the sparingly soluble neutral [bibasic salt]. In this respect, comenic acid is opposite to meconic acid, the acid potash-salt of which is the less soluble of the two. (Robiquet.)

*b. Monobasic.* — The acid dissolved in a slight excess of boiling potash-ley yields crystals on cooling, which, after washing with cold water, crystallise from hot water in short, square, anhydrous needles, which redden litmus. (How.)

| | *Crystals.* | | How. |
|---|---|---|---|
| 12 C | 72·0 | 37·08 | 37·07 |
| 3 H | 3·0 | 1·54 | 1·75 |
| KO | 47·2 | 24·30 | 13·88 |
| 9 O | 72·0 | 37·08 | 47·30 |
| $C^{12}H^3KO^{10}$ | 194·2 | 100·00 | 100·00 |

*Comenate of Soda.* — *Monobasic.* The solution of the acid in tolerably strong boiling soda-ley yields, on cooling, nodules and prisms, which, when washed with a small quantity of cold water, crystallise from solution in the smallest possible quantity of boiling water, in acid, anhydrous four-sided prisms. These crystals dissolve readily in water, and contain 17·09 p. c. soda, and are therefore $C^{12}H^3NaO^{10}$. (How.)

*Comenate of Baryta.* — *a. Bibasic.* — Chloride of barium mixed with a solution of the acid in excess of ammonia, throws down immediately, or in very dilute solutions, after some time only, yellowish quadratic needles united in concentric groups. These crystals do not lose water at 100°, but at 121°, they give off 19·03 p. c. 6 (At.) water, and if then heated to redness in the air, burn away in a fiery cloud. They do not dissolve in boiling water, but when boiled with it, are converted into a basic salt, which does not give off water at 121°, and contains 54·5 p.c. baryta. (How.)

| | *At* 121°. | | How. |
|---|---|---|---|
| 12 C | 72·0 | 23·29 | 23·07 |
| 4 H | 4·0 | 1·29 | 1·71 |
| 2 BaO | 153·2 | 49·55 | 33·81 |
| 10 O | 80·0 | 25·87 | 41·41 |
| $C^{12}H^2Ba^2O^{10} + 2Aq$ | 309·2 | 100·00 | 100·00 |

*b. Monobasic.* — The free acid does not precipitate baryta-salts. (Stenhouse.) — The salt is produced when baryta is boiled with excess of the acid. — Chloride of barium mixed with a cold-saturated aqueous solution of the crystallised ammonia salt, immediately forms a crystalline precipitate, and with a more dilute solution, gradually deposits transparent rhombs [?]. The acid crystals gradually give off their 20·86 p. c. (somewhat more than 6 At.) water at 100°, and melt at a stronger heat. (How.)

| *Dried at* 100°. | | | How. |
|---|---|---|---|
| 12 C | 72·0 | 32·20 | 31·89 |
| 3 H | 3·0 | 1·34 | 1·71 |
| BaO | 76·6 | 34·26 | 33·81 |
| 9 O | 72·0 | 32·20 | 32·59 |
| $C^{12}H^3BaO^{10}$ | 223·6 | 100·00 | 100·00 |

*Comenate of Strontia.* — The two salts closely resemble the baryta-salts, but are more soluble.

*Comenate of Lime.* — *a. Bibasic.* — The acid supersaturated with ammonia, precipitates from chloride of calcium, if the solutions are saturated, very short prisms which give off 18·20 p. c. (5 At.) water at 121°, and when the solutions are dilute, small shining, crystals, which at 121° give off 31·37 p. c. (11 At.) water. The two kinds of crystals are insoluble in water, but become basic when boiled with water.

| *Dried at* 121°. | | | How. |
|---|---|---|---|
| 12 C | 72 | 33·96 | 34·20 |
| 4 H | 4 | 1·89 | 2·36 |
| 2 CaO | 56 | 26·41 | 26·59 |
| 10 O | 80 | 37·74 | 36·85 |
| $C^{12}H^2Ca^2O^{12} + 2Aq$ | 212 | 100·00 | 100·00 |

*b. Monobasic.* — A mixture of chloride of calcium and a cold-saturated aqueous solution of the crystalline ammonia-salt, quickly deposits transparent, shining, rhombic crystals, which give off their water slowly at 100°, but the whole, amounting to 26·15 p. c. (7 At.), at 121°. They dissolve readily in boiling water, and crystallise therefrom on cooling.

| *Dried at* 121°. | | | How. |
|---|---|---|---|
| 12 C | 72 | 41·14 | 40·83 |
| 3 H | 3 | 1·71 | 1·94 |
| CaO | 28 | 16·00 | 16·02 |
| 9 O | 72 | 41·15 | 41·21 |
| $C^{12}H^3CaO^{10}$ | 175 | 100·00 | 100·00 |

*Comenate of Magnesia.* — *a. Bibasic.* — Sulphate of magnesia forms with the acid saturated with ammonia, especially when the mixture is stirred, hard, closely adhering, crystalline grains consisting of short microscopic needles. These crystals heated to 100°, slowly give off 26·50 per cent. (8 At.) water; and if then kept at 121° for four days, they give off such a quantity [nearly 3 At.], that the residual salt contains 21·30 p. c. magnesia, and is therefore not quite anhydrous. They are not soluble in boiling water. (How.)

| *Dried at* 100°. | | | How. |
|---|---|---|---|
| 12 C | 72 | 35·12 | 35·07 |
| 5 H | 5 | 2·44 | 2·53 |
| 2 MgO | 40 | 19·51 | 19·53 |
| 11 O | 88 | 42·93 | 42·87 |
| $C^{12}H^2Mg^2O^{10} + 3Aq$ | 205 | 100·00 | 100·00 |

*b. Monobasic.* — Crystallises, after a while, from a mixture of sulphate of magnesia with the cold-saturated solution of the crystalline ammonia-salt, in small rhombs, and from more dilute solutions, on evaporation, in larger crystals which are strongly acid, give off 22·08 p. c. (6 At.) water at 116°, and dissolve readily in hot water. (How.)

| *Dried at* 116°. | | | How. |
|---|---|---|---|
| 12 C | 72 | 38·92 | 38·62 |
| 5 H | 5 | 2·70 | 2·97 |
| MgO | 20 | 10·81 | 11·10 |
| 11 O | 88 | 47·57 | 47·31 |
| $C^{12}H^{3}MgO^{10} + 2Aq$ | 185 | 100·00 | 100·00 |

*Comenate of Lead.* — The acid and its ammonia-salt form with neutral acetate of lead a yellowish white granular precipitate, soluble in excess of comenic acid, but not in acetic acid. (Stenhouse.)

| *Dried at* 100°. | | | Stenhouse. |
|---|---|---|---|
| 12 C | 72 | 18·95 | 19·14 |
| 4 H | 4 | 1·05 | 1·16 |
| 2 PbO | 224 | 58·95 | 58·50 |
| 10 O | 80 | 21·05 | 21·20 |
| $C^{12}H^{2}Pb^{2}O^{10} + 2Aq$ | 380 | 100·00 | 100·00 |

A lead-salt examined by Robiquet contains 54·1 p. c. oxide of lead.

*Ferric Comenate.* — Comenic acid imparts a bright red colour to ferric salts. The dark blood-red mixture of ferric sulphate with a cold-saturated solution of comenic acid or its ammoniacal salt, becomes paler by long standing, and deposits small, pitch-black, shining, very hard, nearly tasteless crystals, which grate between the teeth, yield a dark brown powder, and dissolve slowly both in cold and in hot water, forming a pale red solution. (Stenhouse.)

| *Crystals dried at* 100°. | | | Stenhouse. |
|---|---|---|---|
| 24 C | 144 | 34·37 | 35·09 |
| 11 H | 11 | 2·63 | 2·91 |
| $Fe^{2}O^{3}$ | 80 | 19·09 | 18·58 |
| 23 O | 184 | 43·91 | 43·42 |
| $Fe^{2}O^{3},2C^{12}H^{4}O^{10} + 3Aq$ | 419 | 100·00 | 100·00 |

The red mixture of aqueous comenic acid with ferric sulphate, becomes dark yellow at 65° (and gives off carbonic acid: *How*), by conversion of all the sesquioxide of iron into protoxide at the expense of the acid, part of which at first remains undecomposed, so that a fresh portion of ferric sulphate again produces reddening. This colour however disappears when the liquid is digested for 12 hours with excess of ferric sulphate, in consequence of the complete conversion of comenic acid into *another acid;* hence the no longer red liquid deposits small, pale yellow, shining crystals of a ferrous salt (probably ferrous oxalate, as the liquid contains oxalic acid : *How*), which burn away when heated, and dissolve sparingly

in water; the acid of these crystals, extracted by potash, no longer reddens ferrous salts. (Stenhouse.)

*Cupric Comenate.* — The dark green, hot aqueous mixture of cupric sulphate and comenic acid (or the crystallised ammonia-salt, according to How), deposits after a few minutes, elongated pyramids having the colour of Schweinfurt green. When comenate of ammonia is used, a greenish yellow, flocculent precipitate is formed. With cupric acetate and comenic acid, the precipitate is smaller in quantity. (Stenhouse.) There is no monobasic cupric comenate. (How.)

| *Crystals dried at* 100. | | | Stenhouse. |
|---|---|---|---|
| 12 C | 72 | 30·51 | 30·95 |
| 4 H | 4 | 1·69 | 1·83 |
| 2 CuO | 80 | 33·90 | 33·37 |
| 10 O | 80 | 33·90 | 33·85 |
| $C^{12}H^2Cu^2O^{10} + 2Aq$ | 236 | 100·00 | 100·00 |

The acid does not precipitate *corrosive sublimate.* (Stenhouse.)

*Comenate of Silver.* — *a. Bibasic.* — A solution of nitrate of silver is exactly precipitated by comenic acid neutralised with ammonia. The thick yellow precipitate does not detonate when heated. (Liebig.)

| | | | Liebig. | Stenhouse. |
|---|---|---|---|---|
| 12 C | 72 | 19·46 | 19·54 | |
| 2 H | 2 | 0·54 | 0·65 | |
| 2 Ag | 216 | 58·38 | 57·83 | 58·28 |
| 10 O | 80 | 21·62 | 21·98 | |
| $C^{12}H^2Ag^2O^{10}$ | 370 | 100·00 | 100·00 | |

*b. Monobasic.* — The precipitate (white, granular or flocculent, according to Stenhouse), which the free acid produces in solution of nitrate of silver. (Liebig.)

| | | | Liebig. | Stenhouse. |
|---|---|---|---|---|
| 12 C | 72 | 27·38 | | |
| 3 H | 3 | 1·14 | | |
| Ag | 108 | 41·06 | 40·36 | 40·79 |
| 10 O | 80 | 30·42 | | |
| $C^{12}H^3AgO^{10}$ | 263 | 100·00 | | |

Comenic acid dissolves sparingly in hydrated *alcohol,* but is insoluble in absolute alcohol. (How.)

*Conjugated Compound.*

## Ethylocomenic Acid.

$C^{16}H^8O^{10} = C^4H^6O^2,C^{12}H^2O^8$.

How. *Ed. Phil. Trans.* xx, 2, 225; *Ann. Pharm.* 80, 88. — Further. *Ed. N. Phil. J.* 1, 212.

*Vinocomenic acid, Comenovinic acid, Weinkomensäure, Aetherkomensäure.*

*Formation and Preparation.* 1. Dry hydrochloric acid gas is passed through absolute alcohol in which pulverised comenic acid is suspended, till the acid dissolves, which takes place slowly; the clear liquid (which deposits nothing on addition of water), evaporated at a temperature below 100°; the crystalline residue maintained at this temperature, till it no longer smells of hydrochloric acid; and then left to crystallise by cooling from its solution in water at nearly 100°. — 2. Pulverised comenic acid heated with alcohol and iodide of ethyl in a closed vessel to a temperature above 100°, forms a granular deposit consisting of an acid not yet examined, (perhaps Stenhouse's parcomenic acid, p 410) and ethylocomenic acid in needle-shaped crystals, which may be separated and purified by recrystallisation. The same products and not amylocomenic acid are obtained by heating a mixture of comenic acid, alcohol and chloride of amyl, to 150° for 12 hours.

*Properties.* Large square needles, which begin to evaporate at 100°; melt at 135° into a clear brown-red liquid which solidifies again in the crystalline form on cooling; and if kept for a longer time at 135°, sublime in long, flat, unaltered needles having the same composition. Reddens litmus.

| | *Needles.* | | | How. |
|---|---|---|---|---|
| 16 C | | 96 | 52·17 | 52·13 |
| 8 H | | 8 | 4·35 | 4·56 |
| 10 O | | 80 | 43·48 | 43·31 |
| $C^{16}H^8O^{12}$ | | 184 | 100·00 | 100·00 |

*Decompositions.* 1. The acid may be boiled for a short time without alteration, but if boiled for a longer time, it yields free comenic acid. — 2. With aqueous solutions of the fixed alkalies, even in the cold, it very quickly forms salts, and yields free alcohol.

*Combinations.* Easily soluble in water.

When ammoniacal gas is passed through a solution of the acid in absolute alcohol, the *ammonia-salt* is deposited in yellow silky bundles of needles, which give off ammonia in dry air, and almost completely in vacuo over oil of vitriol, and leave ethylocomenic acid.

The acid imparts a deep red colour to *ferric-salts.* — Its *silver-salt* is gelatinous and decomposes very quickly even in the dark.

The acid dissolves very readily in *alcohol.*

Its aqueous solution coagulates albumen. (How.)

*Chlorine-nucleus* $C^{12}Cl^2H^6$.

## Chloralbin.

$C^{12}Cl^2H^6$.

LAURENT. (1841.) *Rev. scient.* 6, 72.

*Preparation.* The expressed crystalline mass of still impure terchlorocarbolic acid (p. 182, prep. 1), is dissolved in cold aqueous ammonia, in alcohol, or better in ether, and the needles of chloralbin which remain undissolved, are purified by crystallisation from boiling ether.

*Properties.* Long, white flexible needles, which melt at 190°, and crystallise in fern-like tufts on cooling; at a stronger heat, the compound sublimes undecomposed in needles. It is inodorous.

| | *Needles.* | | Laurent. |
|---|---|---|---|
| 12 C | 72·0 | 48·39 | 48·5 |
| 2 Cl | 70·8 | 47·58 | |
| 6 H | 6·0 | 4·03 | 4·1 |
| $C^{12}Cl^2O^6$ | 148·8 | 100·00 | |

*Decompositions.* The compound burns, with a sooty, green-edged flame, but only so long as it is held in the flame of a spirit-lamp. It is not attacked by boiling nitric acid, by a boiling mixture of fuming oil of vitriol and strong nitric acid, or by boiling alcoholic potash.

It does not dissolve in water or in hot oil of vitriol.

It dissolves sparingly in boiling alcohol, better in boiling ether, and crystallises from both. (Laurent.)

*Oxychlorine-nucleus* $C^{12}ClH^3O^4$.

## Chlorocomenic Acid.

$C^{12}ClH^3O^{10} = C^{12}ClH^3O^4,O^6$.

HENRY HOW. (1851.) *Ed. Phil. Trans.* xx, 2, 225; *Ann. Pharm.* 80, 90; *Chem. Soc. Qu. J.* 4, 368.

*Preparation.* 1. Chlorine gas is passed through water in which pulverised comenic acid is suspended; and the prisms which separate from the solution after a few hours, washed with cold water and recrystallised from hot water. — 2. Cold water saturated with acid comenate of ammonia acquires, when chlorine gas is passed through it, the colour

of chlorine water, and gradually deposits crystals of chlorocomenic acid, which increase on addition of hydrochloric acid, and may be purified as in (1). The mother-liquor becomes continually browner, and still deposits brown crystals of the acid.

The crystals, which contain 3 At. water, are dried at 100°.

| | *Acid at* 100°. | | How. |
|---|---|---|---|
| 12 C | 72·0 | 37·81 | 37·53 |
| Cl | 35·4 | 18·59 | 18·77 |
| 3 H | 3·0 | 1·57 | 1·79 |
| 10 O | 80·0 | 42·03 | 41·91 |
| $C^{12}ClH^3O^{10}$ | 190·4 | 100·00 | 100·00 |

*Decompositions.* 1. The acid melts when heated, blackens, gives off a large quantity of hydrochloric acid, and at last yields a small crystalline sublimate, probably consisting of paracomenic acid.—2. By nitric acid, it is quickly converted into hydrochloric, carbonic, hydrocyanic and oxalic acid. —3. Its aqueous solution treated with zinc, slowly gives off hydrogen, and afterwards contains hydrochloric acid and oxide of zinc.

*Combinations. Hydrated Chlorocomenic acid.*— The above-mentioned long, colourless, shining, four-sided prisms. They give off 12·47 p. c. (3 At.) water at 100°. They dissolve both in cold and in hot water, more readily than comenic acid.

The *chlorocomenates* resemble the comenates, but dissolve more readily in water.

The monobasic chlorocomenates of ammonia, potash, and soda crystallise readily. The bibasic salts are not obtainable.

The ammonia-salt forms with *chloride of barium* and *chloride of calcium,* bundles of needles which appear more or less quickly according to the degree of concentration;—with *sulphate of magnesia* it gradually forms a few crystals;—and with *cupric sulphate* immediately a crystalline precipitate. — The bibasic chlorocomenates of these bases appear to be all amorphous and insoluble.

The acid colours *ferric salts* deep red, like comenic acid.

*Silver-salt.* — *a. Bibasic.* — The acid dissolved in a slight excess of ammonia forms with nitrate of silver, yellow amorphous flakes which, after drying, resemble clay in appearance, consistence and tenacity. The salt dried at 100° contains 56·85 p. c. silver, and is therefore $C^{12}ClHAg^2O^{10}$. When ignited in the air, it leaves silver together with a small quantity of chloride of silver; when boiled with hydrochloric acid, it remains partly undecomposed. It is insoluble in boiling water, but dissolves in nitric acid, from which, if it be heated with the salt, cyanide of silver separates.

*b. Monobasic.* — The warm aqueous acid added to a solution of nitrate of silver, throws down feathery crystals, which, after washing with cold water separate from boiling water in short shining needles. These crystals give off 4·44 p. c. water at 100°. When ignited, they leave silver and chloride of silver.

| | *Dried at* 100°. | | | How. |
|---|---|---|---|---|
| 12 C | 72·0 | .... | 24·21 | |
| Cl | 35·4 | .... | 11·90 | |
| 2 H | 2·0 | .... | 0·67 | |
| AgO | 116·0 | .... | 39·01 | ........ 39·03 |
| 9 O | 72·0 | .... | 24·21 | |
| $C^{12}ClH^{2}AgO^{10}$ | 297·4 | .... | 100·00 | |

Chlorocomenic acid dissolves very readily in warm *alcohol.* (How.)

*Oxybromine-nucleus* $C^{12}BrH^{3}O^{4}$.

## Bromocomenic Acid.

$$C^{16}BrH^{3}O^{10} = C^{12}BrH^{3}O^{4},O^{6}.$$

HENRY HOW. (1851.) *Ed. Phil. Trans.* xx, 2, 225; *Ann. Pharm.* 80, 85; *Chem. Soc. Qu. J.* 4, 369.

*Formation* (p. 384).

*Preparation.* The colourless solution of comenic acid in a slight excess of bromine-water, deposits, after a few hours, shining crystals, which are washed with cold water, recrystallised from boiling water, and freed from water of crystallisation by drying at 100°.

| | *Acid at* 100°. | | | | How. |
|---|---|---|---|---|---|
| 12 C | 72 | .... | 30·64 | ........ | 30·75 |
| Br | 80 | .... | 34·04 | ........ | 34·15 |
| 3 H | 3 | .... | 1·28 | ........ | 1·49 |
| 10 O | 80 | .... | 34·04 | ........ | 33·61 |
| $C^{12}BrH^{3}O^{10}$ | 235 | .... | 100·00 | ........ | 100·00 |

*Decompositions.* 1. The acid is decomposed by nitric acid, yielding hydrobromic, carbonic, hydrocyanic and oxalic acid. — 2. With zinc and water, it decomposes like chlorocomenic acid.

*Combinations. Hydrated Bromocomenic acid.* — Oily, colourless, shining, strongly refracting, four-sided prisms, which dissolve in water less easily than chlorocomenic acid.

The *monobasic bromocomenates* of *ammonia, potash* and *soda* are crystallisable; the first crystallises in long needles. The bibasic salts of these bases are not obtainable.

The *bibasic bromocomenates* of *baryta* and *lime* are amorphous and insoluble; the monobasic salts very easily soluble.

The solution of the acid in a slight excess of ammonia forms with nitrate of silver, the *bibasic bromocomenate of silver* in the form of a yellow precipitate having the consistence of clay when dry; and the solution of the acid in warm water, forms with nitrate of silver, flakes of

*monobasic bromocomenate of silver*, which, after washing with cold water and solution in boiling water, separates in short shining prisms, containing, when dried at 100°, 33·64 p. c. oxide of silver, and therefore $= C^{12}BrH^2AgO^{10}$.

The acid is less soluble in hot alcohol than chlorocomenic acid. (How.)

*Oxyazo-nucleus* $C^{12}NH^5O^2$.

## Comenamic Acid.

$C^{12}NH^5O^8 = C^{12}NH^5O^2,O^6$.

Henry How. *Ed. Phil. Trans.* xx, 2, 225, *Ann. Pharm.* 80, 91; *Chem. Soc. Qu. J.* 4, 370.

*Formation and Preparation.* 1. Monobasic comenate of ammonia heated in a sealed tube to 199°, leaves a carbonaceous mass from which water extracts comenamate of ammonia, the acid of which is precipitated by hydrochloric acid in white scales.—2. Aqueous comenic acid is boiled with excess of ammonia till nearly all the ammonia is expelled from the liquid, which assumes a blackish red colour; the grey, viscid, argillaceous sediment of comenamate of ammonia mixed with colouring matter, collected on a filter, and dissolved in hot water; the solution decomposed by hydrochloric acid not in excess; and the precipitated dark brown scales of impure comenamic acid purified by repeated crystallisation from hot water, and treatment with animal charcoal free from iron. Charcoal containing iron would give a purple colour to the acid.

The crystals are dehydrated by heating to 100°. Their solution reddens litmus strongly.

| *Acid dried at* 100°. | | | | How. |
|---|---|---|---|---|
| 12 C | 72 | .... | 46·45 | ........ 46·16 |
| N | 14 | .... | 9·03 | ........ 9·17 |
| 5 H | 5 | .... | 3·23 | ........ 3·39 |
| 8 O | 64 | .... | 41·29 | ........ 41·28 |
| $C^{12}NH^5O^8$ | 155 | .... | 100·00 | ........ 100·00 |

[The formula $C^{12}AdH^3O^4,O^4$ would represent the acid as monobasic, whereas it is bibasic, like comenic acid.]

The acid is decomposed by boiling with potash, yielding ammonia and comenate of potash.

*Combinations. Hydrated Comenamic acid.* — The above-mentioned crystals: Colourless shining plates which give off 18·81 p. c. (4 At.) water at 100°, and dissolve very sparingly in cold water.

The acid dissolves readily in *hydrochloric* acid and other strong *mineral acids*, and is precipitated therefrom as comenamate of ammonia, when the liquid is not quite neutralised with ammonia.

The acid forms with most bases, *bibasic* and *monobasic salts*.

*Monobasic Comenamate of Ammonia.* — Separates from a slightly acid mixture of the acid with ammonia, on cooling, and from an alkaline solution by evaporation, but not by cooling. Small grains made up of delicate needles, which redden litmus. They are nearly insoluble in cold water, but crystallise from boiling water after some time. Their aqueous solution mixed with a small quantity of ammonia exhibits iridescence by reflected light.

| | *Crystals.* | | How. |
|---|---|---|---|
| 12 C | 72 | 41·86 | 41·56 |
| 2 N | 28 | 16·28 | 16·14 |
| 8 H | 8 | 4·65 | 4·83 |
| 8 O | 64 | 37·21 | 37·47 |
| $C^{12}NH^4(NH^4)O^8$ | 172 | 100·00 | 100·00 |

The *potash* and *soda-salts* crystallise easily and redden litmus.

*Comenamate of Baryta.* — *a. Bibasic* — On mixing a solution of the ammonia-salt containing excess of ammonia with chloride of barium, a heavy white powder is produced, which, after drying in the air, gives off 3·08 p. c. (1 At.) water at 100°, and does not dissolve even in boiling water.

*b. Monobasic.* — The solution of the crystallised ammoniacal salt, mixed with chloride of barium, forms prisms which redden litmus. Also when the aqueous acid is set aside in contact with carbonate of baryta, salt *a* or salt *b* is produced, according to the relative quantities.

| | *Salt a at* 100°. | | How. |
|---|---|---|---|
| 12 C | 72·0 | 23·36 | 22·93 |
| N | 14·0 | 4·54 | |
| 5 H | 5·0 | 1·63 | 1·80 |
| 2 BaO | 153·2 | 49·70 | 50·29 |
| 8 O | 64·0 | 20·77 | |
| $C^{12}NH^3Ba^2O^8 + 2Aq$ | 308·2 | 100·00 | |

| | *Salt b at* 100°. | | How. |
|---|---|---|---|
| 12 C | 72·0 | 29·93 | 30·20 |
| N | 14·0 | 5·82 | |
| 6 H | 6·0 | 2·49 | 2·88 |
| BaO | 76·6 | 31·84 | 31·02 |
| 9 O | 72·0 | 29·92 | |
| $C^{12}NH^4BaO^8 + 2Aq$ | 240·6 | 100·00 | |

*Lime* forms two salts of similar constitution.

The ammonia salt forms with *neutral acetate of lead* a heavy insoluble precipitate.

The deep purple colouring produced by the acid in *ferric salts* is destroyed by mineral acids, but reproduced by water.

The crystallised ammonia-salt forms a grey precipitate with *cupric sulphate.* The ammonia-salt supersaturated with ammonia forms with solution of *nitrate of silver*, a yellowish flocculent, quickly blackening precipitate; and the crystallised ammonia-salt forms a white gelatinous

precipitate, which is partially decomposed by boiling water. The acid dissolves in boiling alcohol of ordinary strength, but scarcely in boiling absolute alcohol. (How.)

¶. *Conjugated Compound.*

## Comenamate of Ethyl.

$C^{16}NH^9O^8 = C^4H^5O,C^{12}NH^4O^7$.

HENRY HOW. *Ed. N. Phil. J.* 1, 212.

*Comenamic Ether.*

When a solution of comenamic acid in absolute alcohol is treated with dry hydrochloric acid gas, and the liquid subsequently evaporated, there remains an oil which dries up at 100° to a solid mass, and when dissolved in alcohol, yields a *hydrochlorate of comenamic ether*, $C^4H^5O,C^{12}NH^4O^7 + HCl + 2HO$; and on treating this compound with oxide of silver, or with ammonia (not in excess), comenamic ether is obtained in needle-shaped crystals containing 2 At. water; $C^4H^5O, C^{12}NH^4O^7 + 2HO$, which they give off at 100°, leaving the anhydrous ether. — When the solid mass above mentioned is treated with water, comenamic acid remains undissolved, and another portion of that acid separates as a crystalline powder from the solution, which contains hydrochloric acid.

The ether is neutral; melts to a yellow liquid when heated, is not altered by ammonia in the cold; and is converted by nitric acid into oxalate of ammonia. It dissolves sparingly in cold *water*, readily in hot water and in *mineral acids*, sparingly in *absolute alcohol*.

A compound of this ether with *hydriodic acid* is obtained by heating iodide of ethyl with a solution of comenamic acid in absolute alcohol to 150° in sealed tubes. (How.) ¶.

*Primary Nucleus* $C^{12}H^{10}$.

## Oil. $C^{12}H^{10}$.

COUERBE. (1838.) *Ann. Chim. Phys.* 69, 184; also *J. pr. Chem.* 18, 165.

*Polycarbure hydrique* (Couerbe).

In the distillation of resin-oil (x, 411), there passes over, after the oil resembling amylene (x, 1, 2) and before the oil $C^{12}H^8$ (xi, 370), the oil $C^{12}H^{10}$, which has a density of 0·7524, boils between 65° and 70°; and a vapour density of 2·637. (Couerbe.)

| | | |
|---|---|---|
| 12 C | 72 | 87·80 |
| 10 H | 10 | 12·20 |
| $C^{12}H^{10}$ | 82 | 100·00 |

| | Vol. | | Density. |
|---|---|---|---|
| C-vapour | 12 | ........... | 4·9920 |
| H-gas | 10 | ........... | 0·6930 |
| Oil-vapour | 2 | ........... | 5·6850 |
| | 1 | ........... | 2·8425 |

The analysis, which is not given, approaches rather to the formula $C^{14}H^{11}$. (Couerbe.)

[The boiling point of $C^{12}H^{10}$, calculated by Gerhardt's method (vii, 57), is 65°.]

## Valerol.

$$C^{12}H^{10}O^2 = C^{12}H^{10},O^2.$$

Gerhardt & Cahours. (1841.) *N. Ann. Chim. Phys.* 1, 62.
Gerhardt. *N. Ann. Chim. Phys.* 7, 275; also *Ann. Pharm.* 45, 29; abstr. *Compt. rend.* 14, 832; *J. pr. Chem.* 27, 124.

*Sources.* Valerian oil obtained by distilling the root of *Valeriana off.*, is a mixture of valerol, valerianic acid (which, according to Gerhardt, is produced, together with some resin, from the valerol), borneene $C^{20}H^{16}$, and borneol $C^{20}H^{18}O^2$ which is gradually produced from it by exposure to moist air.

*Preparation.* Valerian oil is quickly distilled, best in a stream of carbonic acid gas; the last portion, which passes over after the more volatile borneene, borneol, and valerianic acid, collected apart; this portion kept for some time at 200°, to volatilise the rest of the borneene; and then cooled to the crystallising point by surrounding it with ice. The product often requires two or three rectifications before it will solidify.

*Properties.* At 0° and a little above, it forms colourless prisms. These, when heated to 20°, become somewhat dull and opaque, and melt into a neutral oil which floats on water, and smells, not like valerian, but somewhat like hay.

| | | | | | Gerhardt. |
|---|---|---|---|---|---|
| 12 C | 72 | .... | 73·48 | ........ | 73·54 |
| 10 H | 10 | .... | 10·20 | ........ | 10·32 |
| 2 O | 16 | .... | 16·32 | ........ | 16·14 |
| $C^{12}H^{10}O^2$ | 98 | .... | 100·00 | ........ | 100·00 |

Metameric with oxide of mesityl (ix, 24).

*Decompositions.* 1. The oil, when exposed to the air, gives off carbonic acid, and is partly converted into valerianic acid, partly resinised.—2. In contact with an excess of *bromine*, it thickens into a brown pitch.—3. With warm *nitric acid*, it gives off nitrous vapours, and forms a yellow resin which floats upon the liquid.—4. From its blood-red solution in oil of vitriol, water separates only a portion of the oil, whilst,

together with sulphuric acid, there remains in solution a conjugated sulphuric acid which forms with lead-oxide a gummy salt, the *sulpho-valerate of lead* which is soluble in water. Valerol is not perceptibly altered by boiling potash-ley; but every drop of the oil poured upon melting hydrate of potash, gives off hydrogen, and solidifies into a mixture of valerate and carbonate of potash :

$$C^{12}H^{10}O^2 + 6HO = C^{10}H^{10}O^4 + 2CO^2 + 6H.$$

*Combinations.* Valerol dissolves sparingly in *water.*

It absorbs *ammoniacal gas* abundantly, but does not appear to form a crystalline compound with it.

It dissolves readily in *alcohol, ether,* and *volatile oils.*

*Oxygen-nucleus* $C^{12}H^8O^2$.

## Guiacic Acid.

$$C^{12}H^8O^6 = C^{12}H^8O^2,O^4.$$

RIGHINI. *J. Chim. med.* 12, 355.
THIERRY. *J. Pharm.* 27, 381; also *Br. Arch.* 28, 55.

*Preparation.* 1. Rasped guiac-wood is exhausted with alcohol; the greater part of the alcohol distilled off from the tincture; the brownish white liquid which remains with the resin made up into a paste with magnesia; the mixture distilled to dryness, whereupon an aromatic water passes over; the residue suspended in water and mixed with sulphuric acid; the white substance thereby separated, dissolved in alcohol, and the acid obtained in needles by evaporating the liquid. (Righini.) — 2. Commercial guiac resin is dissolved in the requisite quantity of warm alcohol; $\frac{3}{4}$ of the filtrate distilled off; the acid yellowish liquid filtered when cool to remove the deposited resin; then neutralised with baryta [to what purpose ?], and evaporated to one-half; the baryta precipitated by sulphuric acid, any excess of which must be carefully removed by means of baryta-water; the filtrate evaporated to a syrup over the water-bath, and the residue frequently shaken up with ether to extract the guiacic acid. On subsequently evaporating the ether, the acid is deposited in nodular masses containing resin, which may be purified by sublimation in small quantities, and at a very gentle heat (in Mohr's apparatus for benzoic acid). (Thierry.) [Is it not thereby converted into guiacene ?]

White shining needles, which dissolve in water more readily than benzoic or succinic acid, and are likewise soluble in alcohol and ether. (Thierry.)

According to Deville's analysis (*Compt. rend.* 19, 137), the guiacic acid obtained by Thierry is $C^{12}H^8O^6$, and is resolved by sublimation into guiacene (x, 411), and carbonic acid $C^{12}H^8O^6 = C^{10}H^8O^2 + 2CO^2$.

According to Franz Jahn (*N. Br. Arch.* 23, 279; 33, 256), the acid which exists in very small quantity in guiac-wood and in somewhat larger quantity in the resin, is not a peculiar acid, but merely benzoic acid. But the experiments on its reactions made with the impure acid

from guiacum are not decisive, and moreover there is no elementary analysis of the acid.

According to L. E. Jonas (*Arch. Pharm.* [?] 69, 20), a peculiar acid (*Guiakharzsäure*) may be obtained in nodular crystals by the action of chlorine on an alcoholic solution of the resin.

## *Oxygen-nucleus* $C^{12}H^{6}O^{4}$.

# Pyrogallic Acid.

$$C^{12}H^{6}O^{6} = C^{12}H^{6}O^{4},O^{2}.$$

SCHEELE. (1786.) *Opusc.* 2, 226.
DEVEUX. *J. Phys.* 42, 401.
BERZELIUS. *Ann. Chim.* 94, 303.
BRACONNOT. *Ann. Chim. Phys.* 46, 206; *Ann. Pharm.* 1, 26; also *N. Tr.* 24; 1, 234.
PELOUZE. *Ann. Chim. Phys.* 54, 378; also *J. Chim. med.* 10, 276; also *Pogg.* 36, 46; also *J. pr. Chem.* 2, 316.
STENHOUSE. *Ann. Pharm.* 45, 1; also *Mem. Chem. Soc. Lond.* 1, 127; also *Phil. Mag. J.* 22, 279.

*Sublimed Gallic acid, Pyrogallsäure, Brenzgallussäure, Acide pyrogallique.*—Originally ragarded as gallic acid purified by sublimation, till Braconnot and Pelouze established its separate identity.

*Formation.* By the dry distillation of gallic acid or tannin.

*Preparation.* 1. Gallic acid is sublimed at a gentle heat. (Berzelius.) The gallic acid or the tannin should not be heated above 220°, because in that case the principal product would be metagallic acid. It is best therefore to distil the acid in a half-filled glass retort in the oil bath with a thermometer inserted. (Pelouze.) 100 pts. of gallic acid yield 11·7 pts. of pyrogallic acid. (Braconnot.) — 2. Finely-pounded gall-nuts are exhausted with cold water; the infusion evaporated; the perfectly dried and well pulverised extract (about 1lb.) spread out uniformly to the depth of half an inch in a cast iron pan 3 or 4 inches deep and 18 inches wide (as in Mohr's process for the preparation of benzoic acid), a sheet of filtering paper pierced with pin-holes tied over it, the whole being surmounted with a conical paper cap from 12 to 18 inches high; and the pan heated for 12 hours in a sand-bath or better in a metal-bath, as exactly as possible to 205°, and at last a little higher. The bibulous paper retains the greater part of the empyreumatic oil, so that 100 pts. of the extract yield 59 pts. of colourless and 44 pts. of slightly coloured laminæ and needles; if the heating is less carefully conducted, not more than half this product is obtained. The coloured crystals may be resublimed (Stenhouse); [compare Grüneberg, *J. pr. Chem.* 60, 479]. — 3. The powder of gall-nuts is carefully heated in a glass retort till the acid is sublimed and empyreumatic oil begins to pass over. (Deveux.)

*Properties.* White, nacreous, thin, often dendritic laminæ and needles. (Berzelius, Pelouze.) Melts without loss of water at 115° (forming a colourless oil which solidifies in a radiated mass on cooling: Gm.), and boils at 210°, giving off colourless vapours which have a slightly pungent odour. (Pelouze.) Tastes bitter (Berzelius); fresh and bitter (Braconnot); as bitter as salicine (Stenhouse). Does not redden litmus (Berzelius, Stenhouse); scarcely (Pelouze); slightly (Braconnot). — This reddening is produced only when the acid has been sublimed at too high a temperature and may therefore be contaminated with a volatile acid. (Stenhouse.) Permanent in the air when dry.

| | *Sublimed.* | | | Berzelius. | | Pelouze. | | Mulder. | | Stenhouse. |
|---|---|---|---|---|---|---|---|---|---|---|
| 12 C ........... | 72 | .... | 57·14 | .... 56·64 | .... | 57·48 | .... | 57·18 | .... | 57·60 |
| 6 H ........... | 6 | .... | 4·77 | .... 5·00 | .... | 4·83 | .... | 4·77 | .... | 4·78 |
| 6 O ........... | 48 | .... | 38·09 | .... 38·36 | .... | 37·69 | .... | 38·05 | .... | 37·62 |
| $C^{12}H^6O^6$........ | 126 | .... | 100·00 | .... 100·00 | .... | 100·00 | .... | 100·00 | .... | 100·00 |

Mulder's acid (*J. pr. Chem.* 48, 91) was obtained by heating tannin to 250°. Campbell & Stenhouse prefer the formula $C^8H^4O^4$.

*Decompositions.* 1. The acid, when gently *heated,* volatilises for the most part undecomposed, leaving an inconsiderable carbonaceous residue. (Gm.) By repeated sublimation, it is for the most part decomposed, leaving a substance resembling tannin [metagallic acid], together with charcoal. (Braconnot.) It blackens strongly at 250°, giving off water and leaving metagallic acid. (Pelouze). — 2. When quickly heated in contact with the air, it burns with a red flame, without leaving charcoal. (Gm.) — 3. When dissolved in water, or moistened with water, and exposed to the air for a few seconds, it forms a mouldy substance. (Gm. Braconnot.) The solution abandoned to spontaneous evaporation no longer leaves crystals, but a reddish gum. (Stenhouse.) Serves for dyeing the hair (Wimmer, *Repert.* 83, 82.) — 4. Pyrogallic acid dissolved in aqueous alkalis, absorbs oxygen, unless that gas is most carefully excluded, and forms solutions, which are variously coloured according to the nature and quantity of the alkali, and ultimately turn brown, a mouldy substance and perhaps also acetic acid being formed at the same time. — 126 pts. (1 At.) of the acid mixed with ammonia, absorb 48 pts. (6 At.) of oxygen, and form a brown liquid from which hydrochloric acid precipitates mouldy flakes without any evolution of gas. (Döbereiner, *Gilb.* 72, 203; 74, 410). — The solution formed with potash-ley turns brown from above downwards, and leaves, when evaporated in vacuo, a black gum, without crystals, which dissolves readily in water, gives off carbonic and acetic acids when treated with dilute sulphuric acid, and if somewhat concentrated, deposits a few black flakes, which immediately redissolve when washed with cold water. (Stenhouse.) — The shades of colour are as follows: With a small quantity of *ammonia:* yellow; with a large quantity: red-brown. With a small quantity of *potash:* red-brown, afterwards brown; with a large quantity: blackish violet, changing to dark brown. With a small quantity of *baryta*-water or *strontia*-water: reddish yellow; with a large quantity: violet, afterwards brown with brown flakes. With a large quantity of *lime*-water: violet, changing quickly to purple, and ultimately to brown with brown flakes; this effect is produced, though less quickly, even when the air is completely excluded,

because the lime-water contains air which it has absorbed; hence on repeatedly admitting fresh quantities of air, the three colourings are repeated, the brown becoming continually darker. (Gm.) A solution of pyrogallic acid in potash is recommended by Liebig, (*Ann. Pharm.* 66, 107; *Chem. Soc. Qu. J.* 4, 221) as an agent for absorbing oxygen in eudiometric experiments.

5. *Chlorine* gas passed through the aqueous solution of the acid forms hydrochloric acid and colours the liquid hyacinth-red. (Stenhouse.)

6. Pyrogallic acid dissolves in fuming nitric acid, with considerable hissing and rise of temperature, and forms a dark yellow liquid, which is coloured brown by ammonia. (Gm.)

7. Oil of vitriol neither decomposes nor colours the acid at a gentle heat. (Braconnot.) The solution when heated gives off sulphurous acid, turns brown-black, and if afterwards mixed with water, becomes decolorised and deposits carbonaceous-flocks. (Gm.) Dilute sulphuric acid colours the acid [when heated ?], first red, and then black. (Stenhouse.) — 8. The acid immediately precipitates *gold* and *silver* from their solutions in the metallic state. (Gm., Braconnot, Stenhouse.) It reduces *platinum-salts* to the metallic state. (Stenhouse.) With bichloride of platinum it forms a dark-brown mixture, from which a brown transparent, thickish mass is gradually precipitated. (Gm.) From *mercurous* nitrate, it immediately reduces all the mercury. (Braconnot). — With *mercuric* nitrate, it forms a brown, thick, non-metallic precipitate; and with corrosive sublimate, a white cloud probably consisting of calomel. (Gm.) It immediately reduces *ferric* to ferrous sulphate. The dark brown liquid deposits by spontaneous evaporation, crystals of ferrous sulphate mixed with dark brown matter, whence alcohol does not extract any iron, but a sour and rough-tasting mixture of sulphuric acid and tannin, which gives an abundant precipitate with gelatin. (Braconnot.) When the aqueous solution of ferric sulphate is mixed with pyrogallic acid, the sesquioxide of iron is reduced to protoxide, but without evolution of carbonic acid, and a clear liquid is obtained having a fine red colour. (Stenhouse.)

9. To the aqueous solution of bichromate of potash, it immediately imparts a yellowish brown colour, which afterwards changes to dark brown, the liquid at last becoming almost opaque, but without precipitation. (Stenhouse.)

*Combinations.* The acid dissolves in 2·25 pts. of water at 13°. forming a solution which is colourless at first, but quickly turns brown. (Braconnot.) Easily soluble. (Berzelius, Pelouze, Stenhouse.) The fresh solution evaporated in vacuo leaves silvery needles of the anhydrous acid. (Stenhouse.)

The acid dissolves in cold fuming *oil of vitriol,* forming a thick liquid of unaltered colour. (Gm.)

Pyrogallic acid, being but a weak acid, is not capable of separating carbonic acid from the earthy alkalis, but only from ammonia, potash and soda; and it is decomposed in its compounds with the alkalis when exposed to the air; on the other hand, it forms with heavy metallic oxides, insoluble compounds which are more permanent in the air. Many of these oxides it extracts from their solutions in the stronger acids, provided the excess of acid is not too great.

*Pyrogallate of Ammonia.* — The acid dissolved in a small quantity of water, and freed from water and excess of carbonate of ammonia by

evaporation with solid carbonate of ammonia in vacuo over oil of vitriol, leaves a dry yellow or grey salt, which assumes a brown or green colour in contact with the air. (Berzelius.) The acid supersaturated with ammonia gives off all its ammonia in vacuo. (Stenhouse.)

With *potash* or *soda*, out of contact with the air, the acid forms very soluble salts; the potash-salt forms rhombic tables. It does not form a cloud in *baryta* or *strontia* water. (Pelouze.)

*Pyrogallate of Alumina.* — The solution of hydrate of alumina in the aqueous acid is crystallisable; tastes very rough; reddens litmus more strongly than the acid alone; becomes turbid every time it is heated and clear again on cooling; and forms an abundant precipitate with gelatin. (Braconnot.)

The acid imparts a yellow colour to *chloride of titanium* mixed with acetate of ammonia, and then forms a brownish precipitate with it. — It colours *uranic* acetate red-brown, and afterwards throws down a brown precipitate. — It does not alter the following salts either pure or mixed with acetate of ammonia: *Sesquichloride of chromium*, sulphate of *manganese*, sulphate of *zinc*, *proto-sulphate of iron*, sulphate of *cobalt* or sulphate of *nickel*. (Gm.)

The acid forms a white precipitate with tartar-emetic, colours nitrate of *bismuth* yellow, and soon forms a thick brownish yellow precipitate; with *protochloride of tin*, it yields an abundance of white flakes. (Gm.)

*Pyrogallate of Lead.* — *a. Sexbasic.* — Obtained by digesting *b* with strong ammonia. (Berzelius.)

*b. Bibasic.* — The precipitate obtained by mixing a solution of pyrogallate of ammonia in warm water with a boiling solution of nitrate of lead, forms, after washing and drying out of contact with the air, a greyish white crystalline powder, which turns brown after being exposed to the air for a few days. (Berzelius.)

| *Salt a.* | | | Berzelius. |
|---|---|---|---|
| $C^{12}H^6O^6$ | 126 | 15·79 | |
| 6 PbO | 672 | 84·21 | 84·08 |
| $6PbO,C^{12}H^6O^6$ | 798 | 100·00 | |

| *Salt b.* | | | Berzelius. |
|---|---|---|---|
| $C^{12}H^6O^6$ | 126 | 36·0 | |
| 2 PbO | 224 | 64·0 | 63·5 |
| $2PbO,C^{12}H^6O^6$ | 350 | 100·0 | |

The lead-salt obtained by Pelouze exhibited a composition corresponding with that of the salt *b*.

*c. Sesquibasic.* — The acid forms a precipitate with acetate of lead, and, on addition of ammonia, also with the nitrate. (Gm.) — The precipitate obtained by mixing the aqueous acid at the ordinary temperature with excess of acetate of lead, after being quickly washed out of contact with the air, then pressed between paper, and dried in vacuo, is white, with a tinge of yellow. (Stenhouse.)

| | *At* 100°. | | Stenhouse. |
|---|---|---|---|
| 24 C | 144 | 24·49 | 24·51 |
| 12 H | 12 | 2·04 | 2·28 |
| 12 O | 96 | 16·33 | 16·03 |
| 3 PbO | 336 | 57·14 | 57·18 |
| $3PbO,2C^{12}H^6O^6$ | 588 | 100·00 | 100·00 |

According to Stenhouse = $PbO,C^8H^4O^4$.

*Ferroso-ferric Pyrogallate.* — The acid imparts to ferrous sulphate (if it contains ferric oxide, Gm.) a bluish black colour (Braconnot), deep blue, without precipitation. (Stenhouse.) To ferric acetate, or to the hydrochlorate mixed with acetate of ammonia, it communicates a violet-black colour, and afterwards forms a blue-black precipitate; if the iron-salt is in excess, the violet-black colouring gradually passes into brownish green, and afterwards into brown. The violet-black colouring which the acid produces in a solution of ferric hydrochlorate, passes instantly into dark yellowish red (Gm.); confirmed by Wackenroder (*N. Br. Arch.* 27, 274). With a very small quantity of ferric sulphate, however, the acid produces a permanent bluish black colour, because then the pyrogallic acid is not completely decomposed. (Braconnot.) Pyrogallic acid mixed with an alkali, forms a deep blue colour and precipitate with ferric salts. (Pelouze.)

*Cupric Pyrogallate.*— From cupric acetate or cupric sulphate mixed with acetate of ammonia (not from cupric sulphate alone) pyrogallic acid throws down an abundance of brown flakes. (Gm.) The dark brown precipitate quickly turns black; when washed, it dissolves for the most part in the water, forming a colourless liquid, which, in a few minutes becomes dark brown and deposits a new substance. (Stenhouse.)

The acid dissolves in *alcohol* and in *ether*. (Braconnot, Pelouze.) In alcohol however less abundantly than in water. (Stenhouse.)

It does not precipitate gelatin.

## Aconitic Acid.

$C^{12}H^6O^{12} = C^{12}H^6O^4,O^8$.

PESCHIER. (1820.) *N. Tr.* 5, 1, 93; 8, 1, 266.
L. A. BUCHNER. *Repert.* 63, 145.
CRASSO. *Ann. Pharm.* 34, 56.
BAUP. *N. Ann. Chim. Phys.* 30, 312; also *Ann. Pharm.* 77, 293; abstr. *J. pr. Chem.* 52, 52.

*Citridic acid* (Baup).

*Sources.* In various species of *aconite*, as in *Aconitum Napellus* (Peschier); in *Equisetum fluviatile.* (Baup.) Should this statement of Baup prove correct, the maleic acid (viii, 151), which Braconnot & Regnault obtained from equiseta, must be regarded as aconitic acid. The equality in the percentage composition of the two acids may cause the

one to be mistaken for the other; but they are distinguished especially by their behaviour under the influence of heat. Aconitic acid is found also in the herb of *Delphinium consolida* collected after flowering. (Wicke, *Ann. Pharm.* 90, 98.)

*Formation.* 1. By heating citric acid for a short time. (Dahlström, *J. pr. Chem.* 14, 355; Crasso, Baup.) — 2. By the action of water on chloride of aconityl (p. 404). (Pebal.)

*Preparation.* 1. *From Aconitum Napellus.* — The dirty white granular aconitate of lime which is deposited from the extract of the herb, is washed with water and alcohol, and dissolved in water containing a little nitric acid; the filtrate precipitated with acetate of lead; the precipitate well washed, suspended in water and decomposed by sulphuretted hydrogen; the transparent, colourless filtrate evaporated over the water-bath; the residual white crystalline mass dissolved in ether; the resulting solution of the acid filtered from admixed aconitate and a small quantity of phosphate of lime (the residue on the filter treated with acetate of lead in a similar manner yields an additional quantity of the pure acid); the ethereal solution left to evaporate; the remaining acid dissolved in water; and the solution evaporated in vacuo. The acid is then obtained in crystalline crusts, which, before drying should be washed with a small quantity of water to remove the adhering yellowish mother-liquor. (Buchner.) A similar process is adopted by Wicke, for extracting the acid from *Delphinium consolida;* but the colouring matter in this case is very difficult to separate.

2. *From Equisetum fluviatile.*— The expressed juice is decanted from the green sediment, and precipitated with acetate of lead; the copious grey precipitate washed with dilute sulphuric acid and mixed with gelatin to precipitate the tannin; the filtrate saturated with carbonate of lime; the solution evaporated to a syrup, which when left at rest, deposits malate of lime; the liquid separated therefrom decomposed with acetate of lead; the pale grey precipitate decomposed by sulphuric acid; and the filtrate carefully evaporated, and then set aside. In this manner brownish crusts are obtained, which may be purified by repeated crystallisation, treatment with animal charcoal, and solution in ether. (Baup.)

3. *From Citric acid.* — The acid is melted till an empyreumatic odour becomes perceptible and a mass remains which is vitreous after cooling. (Liebig, *Ann. Pharm.* 26, 121.) The dehydrated acid is melted at 155°, or the bihydrated acid kept in a state of fusion till it assumes a brownish yellow colour. (Wackenroder.) — 85 grammes of citric acid are heated in a retort as quickly as the frothing permits, till water and afterwards acetone are evolved, together with carbonic oxide gas, and begin to run down the neck of the retort; the residue when cold dissolved in a small quantity of water, and the solution evaporated till it forms a saline crust; the mass which solidifies on cooling exhausted with ether; the ethereal solution filtered from the citric acid, the greater part of which remains undecomposed; the aconitic acid still containing a certain portion of citric acid, which remains after the evaporation of the ether, dissolved in 5 pts. of absolute alcohol; the solution saturated with dry hydrochloric acid gas, which converts only the aconitic acid into a compound ether; this ether precipitated by water in the form of a heavy oil, and decomposed by alcoholic potash, after separation from the watery mixture; the resulting aconitate of potash dissolved in water and

precipitated by acetate of lead; the well washed lead-precipitate decomposed by sulphuretted hydrogen; and the filtrate evaporated to a syrup which solidifies in the crystalline form. (Crasso.)

The acid exhibits different properties according to its mode of preparation (1), (2) or (3).

*Properties.* (1) White crystalline crusts and nodules consisting of delicate needles (Buchner). (1, 2 and 3) from hot water: white warty crust, and, by very slow crystallisation, transparent four-sided laminæ. (Baup.) (3) White nodules and crusts which melt without decomposition (Crasso.) Pebal obtained the acid in transparent four-sided laminæ by decomposing the chloride of aconityl with water, and also by heating citric acid. (1) Inodorous, pleasantly sour, like citric acid, permanent in the air. (Buchner.)

| | *Crystals.* | | Buchner, at 120°. | Crasso. | Pebal. |
|---|---|---|---|---|---|
| 12 C | 72 | 41·38 | 41·43 | 41·56 | 41·16 |
| 6 H | 6 | 3·45 | 3·62 | 3·81 | 3·46 |
| 12 O | 96 | 55·17 | 54·95 | 54·63 | 55·38 |
| $C^{12}H^{6}O^{12}$ | 174 | 100·00 | 100·00 | 100·00 | 100·00 |

Dahlström (*Repert.* 63, 145) first established by analysis the metamerism of this acid with maleic and fumaric acid.

*Decompositions.* 1. The acid (1) *heated* in a retort turns brown at 130°; melts at 140° forming a red-brown liquid; boils at 160°, and gives off in white fumes, first a pale yellow watery distillate, which deposits a large quantity of delicate prisms, probably of maleic acid (inasmuch as the flocculent precipitate obtained with acetate of lead soon becomes shining and crystalline, and dissolves in water much more readily than aconitate of lead), — and afterwards drops of brown oil having an empyreumatic odour and sharp taste. The residue in the retort is a red-brown viscid, deliquescent mass, whose bitter aqueous solution does not yield any crystals by evaporation. (Buchner.) — The acid (3) heated above its melting point, gives off carbonic acid together with a small quantity of water, then a heavy, strongly acid oil, which solidifies in a crystalline mass on cooling, and consists of itaconic acid (x, 424), mixed with a small quantity of citraconic acid (x, 417): $C^{12}H^{6}O^{12} = C^{10}H^{6}O^{8} + 2CO^{2}$; and leaves a black pitchy mass, which, at a higher temperature, is resolved into empyreumatic oil and tumefied charcoal. (Crasso.) — The acid (1, 2 or 3) melts at a gradually increasing heat, turning brown, and giving off acid vapours, and leaves a tumefied charcoal. (Baup.) — ¶. Aconitic acid heated with water in a sealed tube to 180°, is resolved into itaconic acid and carbonic acid. (Pebal.) — With pentachloride of phosphorus it forms *chloride of aconityl* $C^{22}H^{3}O^{6}Cl^{3}$, together with oxychloride of phosphorus and hydrochloric acid:

$$C^{12}H^{6}O^{12} + 3PCl^{5} = C^{12}H^{3}O^{6}Cl^{3} + 3PCl^{3}O^{2} + 3HCl.$$

The same chloride appears to be obtained by the action of pentachloride of phosphorus on citric acid when the heat is continued for

some time. When treated with water, it reproduces aconitic acid. (Pebal.) ¶.

*Combinations.* (1) dissolves very readily in water, either cold or hot (Buchner); (2) dissolves in 3 pts. of water at 15°, and in a smaller quantity of hot water (Baup); (3) is easily soluble. (Crasso.) The acid from delphinium is also very soluble in water. (Wicke.) The solution is very much inclined to effloresce during evaporation.

*Aconitate of Ammonia.* — *a. Tribasic.* — When prepared with the acid (2), it is not crystallisable. (Baup.) — The acid (1) supersaturated with ammonia and evaporated in vacuo leaves [with loss of ammonia?] a clear, viscid mass which however reddens litmus. (Buchner.)

*b. Bibasic.* — Needles united in warty masses, having a pleasant saline and slightly acid taste. (Buchner.) — The mixture of 1 pt. of the acid (2) neutralised with ammonia, with 1 pt. of the free acid, yields, by very gentle evaporation, crusts consisting of microscopic needles, which may be dried, first on bibulous paper under a bell-jar containing moist air, and then in the open air. The salt dissolves in water more readily than the salt *c*, but is resolved, immediately after solution, into the salt *c* which precipitates in the pulverulent form, and the salts *a* and *b*, which remain in solution. It contains 12·53 per cent. of ammonia. (Baup.)

*c. Monobasic.* — 1 part of the acid is neutralised with ammonia, and 2 pts. more of acid added. Nodules, and by slow crystallisation, transparent laminæ. Dissolves in $6\frac{1}{2}$ pts. of water at 15°, and in a smaller quantity of hot water. Contains 8·84 p. c. ammonia. (Baup.) Therefore $C^{12}H^5(NH^4)O^{12}$.

*Aconitate of Potash.* — *a. Tribasic.* — Gummy, having a not unpleasant saline taste, neutral, becoming moist. (Buchner.)

*b. Bibasic.* — The solution of the salt *a* mixed with only so much acid as to leave a portion of that salt unaltered, is left to crystallise, the mother-liquor containing the salt *a* being continually mixed with additional quantities of acid. When 1 pt. of the acid is neutralised with potash, another 1 pt. of acid added, and the liquid evaporated to the crystallising point, crystals are at first formed containing more acid than the salt *b*, and afterwards the salt *b* is deposited from the mother-liquor. — Transparent, four-sided tables, permanent in the air, or very flat prisms containing 29·16 per cent. of potash. As Baup has not determined the amount of water, his statement that the salt is $KO, 2C^4HO^3,2HO$, cannot be received without further confirmation. The same remark applies to the other aconitates, all of which he supposes to contain $MO, 2C^4HO^3 + 2HO$, that is to say 3 At. base to 2 At. acid ($C^{12}H^6O^{12}$), and not 2 : 1. — The salt dissolves in water more readily than *c*, but is then immediately resolved into the salt *c*, which, if from 3 to 4 pts. of water are present, is precipitated as a crystalline powder, and the salts *a* and *b* which remain in solution. (Baup.)

*c. Monobasic.* — 1 pt. of the acid neutralised with potash and mixed with 2 pts. more of acid, yields small transparent laminæ united in concentric groups, which after a while become opaque, without loss of weight, and may likewise be heated without loss to 100°, and even till they begin to turn yellow. They contain 22·40 per cent. of potash, and are therefore $KO,3C^4HO^3,2HO$ [$= C^{12}H^5KO^{12}$]. They dissolve in 11 pts. of water at 15°, in a smaller quantity of hot water; the solution turns yellow when boiled and yields yellowish crystals. (Baup.)

*Aconitate of Soda.* — *a. Tribasic.* — The salt prepared with acid (1) crystallises with difficulty, generally forming only a moist crystalline crust, which dissolves very readily in water. (Buchner.) Non-crystalline, hygroscopic, insoluble in alcohol.

*b. Bibasic.* — When 1 pt. of the acid neutralised with soda is mixed with 1 pt. of the free acid, and the liquid sufficiently concentrated, the salt is obtained in micaceous laminæ on addition of alcohol, or as a crystalline powder by evaporation. The crystals effloresce in the air, and then contain 20·54 per cent. of soda. (Baup.)

*Aconitate of Baryta.* — *Tribasic.* — The acid forms with baryta-water, and aconitate of ammonia forms with baryta-salts, a gelatinous precipitate which does not become crystalline, and wastes considerably in drying. The salt dried in the cold over oil of vitriol, gives off 13·75 per cent. of water at 140°; when dried at 110°, it contains 60·19 p. c. and at 200° (which temperature it bears without turning brown) it contains 60·54 p. c. baryta [therefore $C^{12}H^{3}Ba^{3}O^{12}$]. It dissolves in aqueous aconitic acid. (Buchner.)

*Aconitate of Lime.* — *Tribasic.* — Occurs in *Aconitum* and in *Delphinium*. Lime-water does not become turbid when mixed with the acid, even if heated. — The aqueous acid saturated with carbonate of lime or aqueous aconitate of soda mixed with chloride of calcium, yields on evaporation, transparent, colourless prisms, which when once formed, re-dissolve but slowly. (Buchner.) The solution of lime in the acid left at rest and gently heated, evaporates to a syrup, which, when exposed to the air, forms gelatinous protuberances in the middle of the basin, and finally dries up to a fissured gum. If, on the other hand, lumps of the crystallised salt be introduced into the evaporating liquid, it yields delicate crystals, soluble in 99 pts. of water at 15°. These crystals give off the greater part of their water at 100°, and the whole at a somewhat higher temperature, turning brown at the same time; they then contain 29·47 p. c. lime. (Baup.) [$= C^{12}H^{3}Ca^{3}O^{12}$.] The salt obtained from extract of aconite, when purified by washing with cold water, and crystallisation from boiling water, forms rhombic crystals; exhibits, when dissolved in boiling water, a slight alkaline reaction; and on being heated, first gives off water, then turns brown, blackens, and swells up, emitting vapours which smell like burnt tartar, and dissolves quietly in dilute nitric acid. (Reinsch, *Ann. Pharm.* 58, 396.)

Aconitate of soda does not precipitate sulphate of *magnesia* or sulphate of *zinc*.

*Aconitate of Manganese.* — *Tribasic.* — The acid boiled continuously with carbonate of manganese, yields, after filtration, evaporation and recrystallisation, small, rose-coloured, transparent, octohedrons, which are permanent in the air, contain 29·54 p. c. protoxide of manganese, give off somewhat more than 29 per cent. of water when heated, and dissolve sparingly in cold water, more readily in lukewarm water, and, with some turbidity (removable by addition of acid), in boiling water. (Baup.)

| | *Crystals.* | | Baup. |
|---|---|---|---|
| $C^{12}H^{3}O^{9}$ | 147 | 40·80 | |
| 3 MnO | 108 | 29·75 | 29·54 |
| 12 HO | 108 | 29·45 | 29·00 |
| $C^{12}H^{3}Mn^{3}O^{12} + 12Aq$ | 363 | 100·00 | |

*Aconitate of Lead.* — *Tribasic.* — The acid and its soda-salt form, with acetate of lead, a white, finely flocculent, non-crystallising precipitate, which, after drying over oil of vitriol at the ordinary temperature, gives off 5·15 p. c. [3 At. ?] water at 140°, and then contains 68·85 p. c. oxide of lead [$C^{12}H^3Pb^3O^{12}$]; it may be heated to 150° without decomposition, and when boiled with water, contracts to a certain extent, and dissolves but very sparingly; the solution does not yield crystals on cooling. (Buchner.) The acid does not precipitate nitrate of lead till partially neutralised. (Baup.)

The acid imparts a reddish colour to ferric salts, and alkaline aconitates added to solutions of these salts, throw down reddish gelatinous flakes. (Buchner, Baup.)

*Cupric Aconitate.* — The beautiful green solution of cupric carbonate in the aqueous acid yields a blue-green crystalline mass when evaporated. The solution, when boiled, deposits part of the copper in the form of brown-red cuprous oxide, whilst the other portion remains dissolved in the acid altered by oxidation. (Buchner.)

*Mercurous Aconitate.* — The acid (Baup), and its soda-salt (Buchner), form a white precipitate with mercurous nitrate.

*Mercuric Aconitate.* — The solution of mercuric aconitate in the warm acid yields on evaporation a white sparingly soluble powder; when boiled for some time, it decomposes and turns grey. (Buchner.)

*Aconitate of Silver.* — Aconitate of ammonia precipitates nitrate of silver (Buchner); but the free acid does not; at all events, partial neutralisation of the acid is necessary to insure precipitation. (Baup.) The white pulverulent precipitate (soft, according to Liebig), blackens on exposure to light. In the dry state, it may be heated without alteration to 150°, but then explodes with violence, giving off brown vapours, and leaving silver containing charcoal; but when moist, it decomposes even at 100°, the silver being reduced in the form of a black powder. (Buchner.) When heated, it burns with a kind of detonation, and throws out cauliflower-like excrescences. (Liebig, Crasso.) When boiled with water, it is converted, without formation of gas, into a sparingly soluble compound of silver-oxide with a peculiar crystallisable acid. The unaltered precipitate likewise dissolves sparingly in water; it dissolves readily in alcohol and ether, and effloresces therefrom in dendritic forms when evaporated. (Buchner.)

| | | | Liebig. | Buchner. | Crasso. | Wicke. |
|---|---|---|---|---|---|---|
| 12 C | 72 | 14·54 | 14·60 | 14·85 | 14·71 | |
| 3 H | 3 | 0·61 | 1·00 | 0·68 | 0·69 | |
| 3 AgO | 348 | 70·30 | 67·07 | 69·51 | 69·21 | 69·57 |
| 9 O | 72 | 14·55 | 17·33 | 14·96 | 15·39 | |
| $C^{12}H^3Ag^3O^{12}$ | 495 | 100·00 | 100·00 | 100·00 | 100·00 | |

The acid dissolves readily in *alcohol* and *ether* (Crasso); in 2 pts. of 88 per cent. alcohol of 12°. (Baup.)

*Conjugated Compound.*

## Aconitate of Ethyl.

$$C^{24}H^{18}O^{12} = 3C^{4}H^{5}O,C^{12}H^{3}O^{3}.$$

The solution of the acid in 5 pts. of absolute alcohol, saturated with hydrochloric acid gas, and mixed with water, deposits the aconitic ether, in the form of an oil.

Colourless oil of sp. gr. 1·074 at 14°, boiling at 236°, having an aromatic odour, like that of *calamus*-oil, and an extremely bitter taste.

When heated in a retort above its boiling point, it decomposes for the most part, giving off thick white fumes, which contain but little of the ether, and leaving a black fatty matter. (Crasso, *Ann. Pharm.* 34, 57.) The ether becomes pitchy after chlorine gas has been passed through it for a few days. (Malaguti, *N. Ann. Chim. Phys.* 16, 84.)

| | | | Crasso. |
|---|---|---|---|
| 24 C | 144 | 55·81 | 55·34 |
| 18 H | 18 | 6·98 | 7·33 |
| 12 O | 96 | 37·21 | 37·33 |
| $C^{24}H^{18}O^{12}$ | 258 | 100·00 | 100·00 |

## ¶. Aconitanilic Acid.

$$C^{24}NH^{9}O^{8} = C^{12}(C^{12}H^{5}O^{4})NH^{4},O^{4}\ ?$$

L. Pebal. *Ann. Pharm.* 98, 83.

*Acide phenyl-aconitamique, Aconitomonanilsäure.*

Obtained by adding water to the product of the action of pentachloride of phosphorus on citranilic acid. Probably thus:

$$\underbrace{C^{24}NH^{11}O^{10}}_{\text{citranilic acid.}} + 2PCl^{5} = C^{24}NH^{8}O^{6},Cl + 2PCl^{3}O^{2} + 3HCl;$$

and:

$$C^{24}NH^{8}O^{6},Cl + 2HO = C^{24}NH^{9}O^{8} + HCl.$$

The chloride $C^{24}NH^{8}O^{6}Cl$ has not been isolated.

When 1 At. citranilic acid is mixed with 2 At. pentachloride of phosphorus, added successively, and the action alternately assisted by a gentle heat, the whole dissolves forming a yellow liquid; and on treating this liquid with water, hydrochloric acid is evolved, and aconitanilic acid separates, in the form of a soft substance, which, by solution in hot water and cooling, may be obtained in small yellow needles, but cannot be decolorised, even by repeated crystallisation from water and dilute alcohol.

| Dried over oil of vitriol. | | | | Pebal. | |
|---|---|---|---|---|---|
| 24 C | 144 | 62·34 | 62·18 | | 62·32 |
| N | 14 | 6·06 | | | 6·02 |
| 9 H | 9 | 3·90 | 4·16 | | 4·05 |
| 8 O | 64 | 27·70 | | | 27·61 |
| $C^{24}NH^9O^8$ | 231 | 100·00 | | | 100·00 |

$$= C^{12}NH^7 + C^{12}H^6O^{12} - 4HO.$$

The acid yields by combustion 30·42 vol. $CO^2$ to 1·26 vol. N, or 24·1 vol. $CO^2$ to 1 vol. N.

The acid dissolves sparingly in *water*, easily in *alcohol*, and very easily in dilute aqueous ammonia, forming a purple solution.

*Silver-salt*, $C^{24}NH^8AgO^8$. — Nitrate of silver added to the ammoniacal solution of the acid, throws down rose-coloured flakes, which, when washed with water, pressed between paper, and dried over oil of vitriol, contain 31·83 p. c. silver.

When the liquid formed by the action of pentachloride of phosphorus on citranilic acid, and containing the chlorine compound $C^{24}NH^4O^6Cl$, is mixed, drop by drop, with aniline, and the product exhausted with alcohol, a yellow powder is obtained, which, when recrystallised from hot alcohol, yields crystals of aconitobianil:

$$C^{24}NH^8O^6Cl + C^{12}NH^7 = C^{36}N^2H^{14}O^6 + HCl.$$

## ¶. Aconito-bianil.

$$C^{36}N^2H^{14}O^6 = C^{24}(C^{12}H^5O^4)N^2H^9,O^2. ?$$

L. Pebal. *Ann. Pharm.* 98, 79.

*Phenyl-aconitimide.*

*Formation and Preparation.* 1. By the action of aconitic acid upon aniline:

$$C^{12}H^6O^{12} + 2C^{12}NH^7 = C^{36}N^2H^{14}O^6 + 6HO.$$

1 At aconitic acid is heated with 3 At. aniline to 130° or 140°; and the resulting soft mass is boiled with dilute hydrochloric acid to remove excess of aniline; then left to cool; pulverised; digested for some time with cold dilute hydrochloric acid; washed on a filter with water; pressed, and finally treated with cold alcohol. A brown-red solution is then formed which leaves a brown amorphous mass (aconitalinide?) when evaporated, and a yellow residue is left, which dissolves in a large quantity of boiling alcohol, and on cooling yields straw-yellow needles of aconito-bianil. — 2. By the action of oxychloride of citryl on aniline:

$$C^{12}H^8O^{12}Cl^2 + 2C^{12}NH^7 = C^{36}N^2H^{14}O^6 + 6HO + 2HCl.$$

Aniline added in drops to oxychloride of citryl, acts with great violence, forming black products of decomposition. But when the oxychloride is sprinkled in fine powder and by small portions into aniline, the mass being

stirred all the while, and the action of the oxychloride being continued as long as any action takes place, a viscid mass is at length obtained which may be heated in the oil-bath without further decomposition. On treating the cooled mass with dilute hydrochloric acid and boiling it with water to remove excess of aniline and hydrochlorate of aniline, a residue is obtained which melts below 100°, and yields on cooling a brown amorphous mass, consisting of aconitanilide (?) and aconito-bianil, which may be separated by alcohol as before.

*Properties.* Slender needles of a pale straw-yellow colour, insoluble in water, slightly soluble in alcohol.

| | *Dried over oil of vitriol.* | | | Pebal. | |
|---|---|---|---|---|---|
| 36 C | 216 | .... 70·59 | .... | 70·50 | .... 70·55 |
| 2 N | 28 | .... 9·15 | .... | | .... 9·29 |
| 14 H | 14 | .... 4·57 | .... | 4·77 | .... 4·77 |
| 6 O | 48 | .... 15·69 | | | |
| $C^{36}N^2H^{14}O^6$ | .... 306 | .... 100·00 | | | |

Boiling aqueous ammonia acts but slowly on this compound; but when the two bodies are heated together in a sealed tube, a yellowish solution is obtained, from which hydrochloric acid throws down a reddish white flocculent precipitate, which dissolves sparingly in water, readily in ammonia and in alcohol, and probably consists of *aconito-bianilic acid.* ($C^{36}N^2H^{14}O^6 + 2HO = C^{36}N^2H^{16}O^8$.) Nitrate of silver added to the ammoniacal solution of this substance, forms a precipitate which blackens very quickly.

*Aconitanilide.* $C^{48}N^3H^{21}O^6$? The brown amorphous substance extracted by cold alcohol from the product of the action of aconitic acid or oxychloride of citryl on aniline (p. 409), dissolves partially in ammonia, and the residue yields [by combustion with oxide of copper], a mixture of 45·6 vol. carbonic acid to 3 vol. nitrogen; hence it is probably aconitanilide, the formation of which may be represented by the equations:

$$C^{12}H^6O^{12} + 3C^{12}NH^7 = C^{48}N^3H^{21}O^6 + 6HO;$$

and:

$$C^{12}H^8O^{12}Cl^2 + 3C^{12}NH^7 = C^{48}N^3H^{21}O^6 + 6HO + 2HCl. ¶.$$

*Oxygen-nucleus* $C^{12}H^4O^6$.

## Paracomenic Acid.

$$C^{12}H^4O^{10} = C^{12}H^4O^6,O^4. ?$$

STENHOUSE. *Phil. Mag. J.* 24, 132; also *Ann. Pharm.* 49, 25; also *J. pr. Chem.* 32, 262.

*Pyrocomenic acid.* — First observed by Gruner & Robiquet, regarded as reproduced comenic acid by Gregory, and somewhat more exactly investigated by Stenhouse.

When meconic or comenic acid is subjected to dry distillation, paracomenic acid sublimes after the pyromeconic acid, in very small quantity and in feathery crystals; it is best obtained in Mohr's benzoic acid apparatus at a heat not quite sufficient to char the paper. At this temperature, the greater portion of the pyromeconic acid is destroyed or volatilised, while in the cup and on the paper cover, there are deposited, together with a small quantity of pyromeconic acid, dark yellow crystals of paracomenic acid, which, by solution in hot water, boiling with animal charcoal, filtration and cooling, are converted into hard crystalline grains of a very pale yellow colour, having a very strong acid taste and reaction, and assuming a pale red colour when slowly dried. (Stenhouse.)

| *Crystals at* 100°. | | | Stenhouse. |
|---|---|---|---|
| 12 C | 72 | 46·15 | 46·63 |
| 4 H | 4 | 2·57 | 2·71 |
| 10 O | 80 | 51·28 | 50·66 |
| $C^{12}H^4O^{10}$ | 156 | 100·00 | 100·00 |

Isomeric with comenic acid.

*Primary-nucleus* $C^{12}H^{12}$.

## Caproene. $C^{12}H^{12}$.

E. Fremy. (1837.) *N. Ann. Chim. Phys.* 65, 139.

*Caprylene, Oleene* (Fremy); *Prone* (Gm.).

*Formation.* In the dry distillation of most fatty bodies.

*Preparation.* The oily mixture of caproene and pelargonene, $C^{18}H^{18}$ obtained by the dry distillation of hydroleic or metaoleic acid, is freed from the admixed less volatile empyreumatic oil by distillation, then from the volatile acids by agitation with weak potash-ley, and from water by setting it aside for several days in contact with chloride of calcium,—and finally separated, by repeated fractional distillation, the first portion being always collected apart, into the more volatile caproene and the less volatile pelargonene.

*Properties.* Thin colourless oil, which floats on water, boils at 55°, has a vapour-density of 2·875, a penetrating nauseating odour somewhat like that of arsenic, and kills birds which breathe its vapour for a short time.

| | | | Fremy. |
|---|---|---|---|
| 12 C | 72 | 85·71 | 85·74 |
| 12 H | 12 | 14·29 | 14·72 |
| $C^{12}H^{12}$ | 84 | 100·00 | 100·46 |

| | Vol. | Density. |
|---|---|---|
| C-vapour | 12 | 4·9920 |
| H-gas | 12 | 0·8316 |
| Vapour of Caproene | 2 | 5·8236 |
| | 1 | 2·9118 |

Caproene burns with a white flame, tinged here and there with green. — With chlorine gas at ordinary temperatures it forms a liquid compound. — It is nearly insoluble in water, but dissolves readily in alcohol and ether. (Fremy.)

## ¶. Caproyl.

$$C^{12}H^{13} \text{ or } C^{24}H^{26} = \begin{cases} C^{12}H^{13} \\ C^{12}H^{13} \end{cases}$$

A. Wurtz. *N. Ann. Chim. Phys.* 44, 275; *Ann. Pharm.* 96, 372.

*Hexyl.*

Occurs (together with propyl, butyl, and amyl) among the products of the destructive distillation of Boghead coal (C. G. Williams, *Proc. Roy. Soc.* 8, 338).

*Formation.* By the electrolysis of œnanthylic acid:

$$[C^{14}H^{14}O^4 = C^{12}H^{13} + H + 2CO^2].$$

*Preparation.* A concentrated solution of 100 grms. œnanthylic and 120 grms. valerianic acid neutralised with pure carbonate of potash, was subjected at 0° to the action of the current of six Bunsen's cells. Bicarbonate of potash then separated, and an oily liquid having a pungent odour rose to the surface of the alkaline solution. On subjecting this oil, after dehydration with chloride of calcium, to fractional distillation, a small portion (probably caproene) passed over below 100°, a second portion (consisting chiefly of butyl) between 100° and 140°, the largest portion (butyl-caproyl) between 140° and 180°, and lastly a portion between 180° and 220°: this portion was chiefly caproyl. (Wurtz.)

*Properties.* Oily liquid of sp. gr. 0·7574. Boils at about 202°, yielding a vapour whose density is 5·983. (Wurtz.) Sp. gr. 0·7568; boiling point 202°; vapour density 5·83. (Williams.)

| | | | Wurtz. |
|---|---|---|---|
| 24 C | 144 | 84·70 | 84·25 |
| 26 H | 26 | 15·30 | 15·49 |
| $C^{24}H^{26}$ | 170 | 100·00 | 99·74 |

| | Vol. | Density. |
|---|---|---|
| C-vapour | 24 | 9·9840 |
| H-gas | 26 | 1·8118 |
| Vapour of Caproyl | 2 | 11·7958 |
| | 1 | 5·8979 |

*Butyl-caproyl.* $C^{20}H^{22} = C^8H^9,C^{12}H^{13}$. — The portion of the preceding distillate which passed over between 140° and 180°, yielded, after repeated fractional distillation, a portion boiling between 150° and 155°, and another between 155° and 160°. The former exhibited a vapour-density of 4·866; the latter of 4·917.

| | | | Wurtz (*mean*). |
|---|---|---|---|
| 20 C | 120 | 84·50 | 84·68 |
| 22 H | 22 | 15·50 | 15·46 |
| $C^{20}H^{22}$ | 142 | 100·00 | 100·14 |

| | Vol. | Density. |
|---|---|---|
| C-vapour | 20 | 8·3200 |
| H-gas | 22 | 1·5246 |
| Vapour of $C^{20}H^{22}$. | 2 | 9·8446 |
| | 1 | 4·9223 |

*Methyl-caproyl.* $C^{14}H^{16} = C^2H^3,C^{12}H^{13}$. — Obtained by the electrolysis of a mixture of acetate and œnanthylate of potash, but in small quantity only, probably because œnanthylic acid is much more easily decomposed by the current than acetic acid. The oily liquid thus obtained was subjected to fractional distillation, and the portion which passed over at 85° collected apart. This was chiefly methyl-caproyl: its vapour-density was found to be 3·426.

| | | | Wurtz (*mean*). |
|---|---|---|---|
| 14 C | 84 | 84 | 84·52 |
| 16 H | 16 | 16 | 15·50 |
| $C^{14}H^{16}$ | 100 | 100 | 100·02 |

| | Vol. | Density. |
|---|---|---|
| C-vapour | 14 | 5·8240 |
| H-gas | 16 | 1·1088 |
| Vapour of $C^{14}H^{16}$. | 2 | 6·9328 |
| | 1 | 3·4664 |

## ¶. Caproic Alcohol.

$$C^{12}H^{14}O^2 = C^{12}H^2,H^2O^2 = \left.\begin{matrix} C^{12}H^{13} \\ H \end{matrix}\right\} O^2.$$

FAGET. *Compt. rend.* 37, 730; *Ann. Pharm.* 88, 325.

*Hydrate of Caproyl, Hydrated oxide of Caproyl, Hydrate of Hexyl.*

Occurs, together with propylic alcohol (ix, 398), and amylic alcohol in the fusel-oil of brandy prepared from wine-lees, and is obtained in an approximately pure state by collecting apart the portion which distils

between 148° and 154°. It is a colourless, aromatic, strongly refracting liquid, insoluble in water, of sp. gr. 0·833 at 0° and 0·754 at 100°. Vapour-density = 3·53.

*Calculation.*

| | | |
|---|---|---|
| 12 C | 72 | 70·59 |
| 14 H | 14 | 13·72 |
| 2 O | 16 | 15·69 |
| $C^{12}H^{14}O^2$ | 102 | 100·00 |

| | Vol. | Density. |
|---|---|---|
| C-vapour | 12 | 4·9920 |
| H-gas | 14 | 0·9702 |
| O-gas | 1 | 1·1093 |
| Vapour of $C^{12}H^{14}O^2$. | 2 | 7·0715 |
| | 1 | 3·5357 |

The alcohol heated with potash gives off hydrogen and is converted into caproic acid.

A specimen of the alcohol contaminated with amylic alcohol gave with sulphuric acid a conjugated acid whose potash-salt (obtained in very small quantity only) yielded 40·4 p. c. sulphate of potash (the formula $C^{12}H^{13}KO^2,2SO^3$ requires 39·6 p. c.—An impure portion of the alcohol, distilling between 154° and 166°, gave when treated with sulphuric acid and bichromate of potash, caproic acid, and an oily liquid which boiled at 160°, had a vapour-density of 7·34, and a composition corresponding with the formula $C^{26}H^{26}O^4$; therefore *caproate of œnanthyl* or *œnanthylate of caproyl.*—[Other portions of the distillate obtained between 166° and 195°, appeared from their vapour-density and composition, to be mixtures of œnanthylic alcohol $C^{14}H^{16}O^2$ and caproic alcohol $C^{16}H^{18}O^2$. (Faget.) ] ¶.

## Caproic Acid.

$$C^{12}H^{12}O^4 = C^{12}H^{12},O^4.$$

CHEVREUL. (1818). *Ann. Chim. Phys.* 23, 22; also *Schw.* 39, 179.— *Recherches sur les corps gras.* 134 and 209.
LERCH. *Ann. Pharm.* 49, 220
FEHLING. *Ann. Pharm.* 53, 406.
J. S. BRAZIER & GEORGE GOSSLETH. *Chem. Soc. Qu. J.* 3, 210; *Ann. Pharm.* 75. 249.

*Capronsäure, Acide caproique.*

*Sources.* In the form of a conjugated compound, in the butter of the cow and goat (Chevreul); in cocoa-nut fat (Fehling); in Limburg cheese, (Iljenko & Laskowsky, *Ann. Pharm.* 55, 78); and was once found in human urinary calculi. (Joss, *J. pr. Chem.* 4, 375.) Found also together with butyric, caprylic and a fatty acid of higher atomic weight, in the

fusel-oil obtained from the fermented molasses of mangold-wurzel. (A. Müller, *J. pr. Chem.* 66, 103.)

*Formation.* 1. By distilling œnanthol or œnanthylic acid with strong nitric acid (Tilley, *Ann. Pharm.* 67, 108); or oleic acid with strong nitric acid (Redtenbacher, *Ann. Pharm.* 59, 41); or the more volatile oil of the distillate obtained from rape-oil with nitric acid (Schneider, *Ann. Pharm.* 70, 112); or poppy-oil with chromic acid (Arzbächer, *Ann. Pharm.* 73, 203); or casein with peroxide of manganese and sulphuric acid. (Gückelberger, *Ann. Pharm.* 64, 39. — 2. By boiling cyanide of amyl with potash. (p. 68; Frankland & Kolbe, *Ann. Pharm.* 69, 303.)

*Preparation. From animal butter.* — For the preparation of the baryta-salt, according to Lerch & Chevreul, vid. x, 80, 81.—To separate the acid, 100 pts. of the baryta-salt are treated in a glass tube with a mixture of 29·63 pts. oil of vitriol and 29·63 pts. water; the separated caproic acid decanted after 24 hours; and an additional portion obtained from the remaining liquid by subsequent addition of the mixture of oil of vitriol and water:—the total product amounting to about 50 parts. The residue neutralised with baryta-water, filtered and evaporated, still yields a small quantity of caproate of baryta. The decanted acid which is free from sulphuric acid, is digested for 48 hours with an equal quantity of chloride of calcium, and then distilled. (Chevreul.)

2. *From Cocoa-nut fat.* — The fat is saponified by soda-ley of sp. gr. at least 1·12; the clear soapy solution distilled somewhat rapidly with sulphuric acid; the distillate containing caproic and caprylic acids neutralised with baryta-water; and the liquid evaporated. The caprylate of baryta then separates first and afterwards the caproate; and both salts may be purified by recrystallisation. (Fehling.)

3. *From Cyanide of Amyl.* — 1 pt. of cyanide of potassium is distilled with 3 pts. of amylosulphate of potash; the portion of the distillate which has passed over between 130° and 150°, and contains fusel-oil, cyanate of ethyl and cyanurate of ethyl, besides cyanide of amyl, boiled for half an hour with alcoholic potash in a retort having its neck directed upwards, so that the greater part runs back again, and ammonia chiefly escapes together with water; and the pasty residue distilled with water, with which also ammonia, alcohol, fusel-oil and amylamine pass over, while caproate of potash remains, and solidifies in the crystalline form on cooling. From the solution of this salt in a small quantity of water, sulphuric acid separates the caproic acid in the form of an oil which rises to the surface. In distilling this oil, the portion which gives over at 198° is to be collected apart as the purest, inasmuch as a certain portion of caproate of amyl is formed by the action of the sulphuric acid on the small quantity of fusel-oil dissolved in the caproate of potash, and this ether gradually raises the boiling point to 211°. (Brazier & Gossleth.)

*Properties.* Transparent, colourless, very thin oil, of sp. gr. 0·922 at 26° (0·931 at 15°, according to Fehling.) Does not solidify at — 9°; boils at a temperature above 100°, and volatilises undecomposed (at 198°, according to Brazier & Gossleth; at 202°, soon rising to 209°, and forming a vapour of sp. gr. 4·26, according to Fehling). Smells like very weak acetic acid, or rather like sweat: has a pungent sour taste with a sweetish after-taste, like nitrous ether, stronger than that of butyric acid; makes the tongue white. Reddens litmus strongly. (Chevreul.)

| | | | Fehling. |
|---|---|---|---|
| 12 C | 72 | 62·07 | 62·25 |
| 12 H | 12 | 10·35 | 10·47 |
| 4 O | 32 | 27·58 | 27·28 |
| $C^{12}H^{12}O^4$ | 116 | 100·00 | 100·00 |

| | Vol. | Density. |
|---|---|---|
| C-vapour | 12 | 4·9920 |
| H-gas | 12 | 0·8316 |
| O-gas | 2 | 2·2186 |
| Acid-vapour | 2 | 8·0422 |
| | 1 | 4·0211 |

Chevreul's original formula was $C^{12}H^{10}O^4$.—The acid heated with protoxide of lead, gives off 8·66 p. c. water. (Chevreul.)

*Decompositions.* 1. The acid when distilled out of contact with the air, behaves like valerianic acid. — 2. It burns like a volatile oil. — 3. Its solution in oil of vitriol blackens slightly at 100°, but at a stronger heat more readily than butyric acid, and when boiled, gives off caproic acid with a small quantity of sulphurous acid, and leaves a carbonaceous residue. (Chevreul.) — 4. A concentrated solution of caproate of potash decomposed by the current of six Bunsen's cells (as at p. 31), gives off hydrogen, carbonic acid, and a gas having an aromatic odour, while the liquid becomes turbid, and an oily mixture boiling between 125° and 160°, and consisting of an acid, probably caproic acid, together with $C^{20}H^{20}$ (Frankland's amyl) rises to the surface, and may be separated by distillation with alcoholic potash. (Brazier & Gossleth).

*Combinations.* 1 pt. of the acid dissolves in 96 pts. of *water* at 7°. (Chevreul.)

Cold *oil of vitriol* dissolves the acid, with evolution of heat; and the acid is partly separated again on addition of water. — Cold *nitric acid* of 35° B. dissolves the acid slowly, and without decomposition. (Chevreul.)

With salifiable bases, it forms the *Caproates.*

*Caproate of Ammonia.* — The acid, like butyric acid, forms with ammoniacal gas, a crystalline, and with a larger quantity of ammonia, a liquid salt. (Chevreul.)

*Caproate of Potash.* — A hot solution of carbonate of potash is neutralised with aqueous caproic acid, and left to evaporate. The liquid solidifies into a very transparent jelly which becomes opaque when heated. (Chevreul.)

| *Dried above* 100°. | | | Chevreul. |
|---|---|---|---|
| $C^{12}H^{11}O^3$ | 107·0 | 69·39 | |
| KO | 47·2 | 30·61 | 29·73 |
| $C^{12}H^{11}KO^4$ | 154·2 | 100·00 | |

*Caproate of Soda.* — Prepared like the potash-salt. The solution solidifies into a white mass by spontaneous evaporation. (Chevreul.)

| | | | | Chevreul. |
|---|---|---|---|---|
| $C^{12}H^{11}O^3$ | 107·0 | .... | 77·43 | |
| NaO | 31·2 | .... | 22·57 | 21·85 |
| $C^{12}H^{11}NaO^4$ | 138·2 | .... | 100·00 | |

*Caproate of Baryta.*—The aqueous solution evaporated in contact with the air below 18°, yields highly lustrous, opaque, six-sided laminæ often united in cockscomb-like tufts, having a fatty lustre after drying, and not diminishing in weight when left over oil of vitriol in vacuo: by evaporating the solution at a temperature above 30°, the salt is obtained in needles. In the moist state, it smells like the acid when exposed to the air; its taste is alkaline and at the same time resembles that of the acid. When moderately heated, it melts without decomposition; at a higher temperature, it gradually blackens, and gives off a strong aromatic odour. At 10·5° it dissolves in 12·46 pts. and at 20° in 12·5 pts. of water. (Chevreul.) The crystals melt at a gentle heat, give off a gas containing hydrocarbons (chiefly $C^6H^6$, according to Hofmann), and a small quantity of nearly colourless oil, the boiling point of which rises from 120° to 170°; this oil appears to be a mixture of caprone (p. 420), and a small quantity of caprol $C^{12}H^{12}O^2$. The more quickly the salt is heated, the greater is the quantity of gas obtained, and the smaller that of the oil, which then also is more strongly coloured; the greater also is the quantity of charcoal which remains behind together with the carbonate of baryta. The salt dissolved in water gives off when boiled, the odour of caproic acid, and deposits a white mass probably consisting of a basic salt. (Brazier & Gossleth.)

| | *Needles.* | | Lerch. | Fehling. | Iljenko & Lask. | Tilley. | Arzbächer. |
|---|---|---|---|---|---|---|---|
| 12 C | 72·0 | 39·22 | 39·44 | 39·06 | 40·04 | 38·83 | 38·92 |
| 11 H | 11·0 | 5·99 | 6·09 | 6·15 | 6·15 | 5·89 | 5·91 |
| BaO | 76·6 | 41·72 | 41·47 | 41·09 | 41·33 | 41·82 | 41·93 |
| 3 O | 24·0 | 13·07 | 13·00 | 13·70 | 12·48 | 13·46 | 13·24 |
| $C^{12}H^{11}BaO^4$ | 183·6 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 |

The salt contains 42 p. c. baryta (Chevreul), 41·72 (Schneider), 41·2 (Frankland & Kolbe), 41·1 (Wrightson).

*Caproate of Strontia.* — The laminæ, which are transparent in the recent state, soon become opaque when exposed to the air. They have the taste of the baryta-salt. The salt after efflorescence, does not lose any thing further at 100°. When heated in a crucible, it melts, and emits a powerful odour like that of the volatile oil of the *Labiatæ.* Dissolves in 11·05 pts. of water at 10°. (Chevreul.)

| *Dried at* 100°. | | | | Chevreul. |
|---|---|---|---|---|
| $C^{12}H^{11}O^3$ | 107 | .... | 67·30 | |
| SrO | 52 | .... | 32·70 | 32·69 |
| $C^{12}H^{11}SrO^4$ | 159 | .... | 100·00 | |

*Caproate of Lime.* — Crystallises in laminæ having a strong lustre, and partly quadratic. Melts when heated, and gives off a strong odour like that of the *Labiatæ.* Dissolves in 49·4 pts. of water at 14°. (Chevreul.)

*Caproate of Magnesia.* $C^{12}H^{11}MgO^4 + Aq$. Crystallises in small needles grouped in tufts. After drying over oil of vitriol, it contains 15·3 p. c. magnesia, corresponding with the above formula. (Wrightson, *Ann. Pharm.* 90, 46.)

Caproic acid unites with *lead-oxide*, producing rise of temperature. With *iron*, it behaves like valerianic acid.

*Caproate of Silver.*—The white curdy precipitate which caproate of baryta forms with nitrate of silver, dissolves sparingly in water and does not crystallise. (Lerch.) The salt dissolved in a large quantity of boiling water, crystallises on cooling, in large laminæ which are not very sensitive to light or heat. (Frankland & Kolbe.)

| | | | Lerch. | Frankland & Kolbe. |
|---|---|---|---|---|
| 12 C | 72 | 32·29 | 32·30 | 32·0 |
| 11 H | 11 | 4·93 | 4·94 | 4·9 |
| AgO | 116 | 52·02 | 51·73 | 52·3 |
| 3 O | 24 | 10·76 | 11·03 | 10·8 |
| $C^{12}H^{11}AgO^4$ | 223 | 100·00 | 100·00 | 100·0 |

The acid dissolves in all proportions in absolute alcohol. (Chevreul.)

*Conjugated Compounds.*

## Caproate of Methyl.

$C^{14}H^{14}O^4 = C^2H^3O,C^{12}H^{11}O^3$.

FEHLING. (1845.) *Ann. Pharm.* 53, 407.

When a solution of 2 pts. of caproic acid in 2 pts of wood-spirit is heated with 1 pt. of oil of vitriol, caproate of methyl rises to the surface; it may then be washed with water and dried over chloride of calcium. Sp. gr. 0·8977 at 18°. Boiling point 150°. Vapour-density 4·623. Odour like that of the caproates, but more unpleasant. (Fehling.)

| | | | Fehling. |
|---|---|---|---|
| 14 C | 84 | 64·61 | 64·42 |
| 14 H | 14 | 10·77 | 10·82 |
| 4 O | 32 | 24·62 | 24·76 |
| $C^{14}H^{14}O^4$ | 130 | 100·00 | 100·00 |

| | Vol. | Density. |
|---|---|---|
| C-vapour | 14 | 5·8240 |
| H-gas | 14 | 0·9702 |
| O-gas | 2 | 2·2186 |
| Vapour | 2 | 9·0128 |
| | 1 | 4·5064 |

## Caproate of Ethyl.

$$C^{16}H^{16}O^4 = C^4H^5O,C^{12}H^{11}O^3.$$

LERCH. (1844.) *Ann. Pharm.* 49, 222.
FEHLING. *Ann. Pharm.* 53, 407.

*Caproic ether.*

*Preparation.* 1. When a solution of 2 pts. of caproic acid in 2 pts. alcohol is heated with 1 pt. of oil of vitriol, the ether rises completely to the surface, and may be washed with water and dried over chloride of calcium. (Fehling.) — 2. When a mixture of caproate of baryta with alcohol and oil of vitriol is heated, caproic ether soon rises to the surface, and may be washed with water, dried with chloride of calcium and distilled. (Lerch.)

*Properties.* Transparent, colourless liquid (Lerch), of sp. gr. 0·882 (Fehling), boiling at 120° (Lerch), at 162° (Fehling); vapour-density 4·965 (Fehling). Smells and tastes like butyrate of ethyl. (Lerch.)

| | | | Lerch. | Fehling. |
|---|---|---|---|---|
| 16 C | 96 | 66·67 | 66·85 | 66·36 |
| 16 H | 16 | 11·11 | 11·07 | 11·22 |
| 4 O | 32 | 22·22 | 22·08 | 22·42 |
| $C^{16}H^{16}O^4$ | 144 | 100·00 | 100·00 | 100·00 |

| | Vol. | Density. |
|---|---|---|
| C-vapour | 16 | 6·6560 |
| H-gas | 16 | 1·1088 |
| O-gas | 2 | 2·2186 |
| Vapour of Caproic ether.. | 2 | 9·9834 |
| | 1 | 4·9917 |

Metameric with caprylic acid.

## Caproate of Amyl.

$$C^{22}H^{22}O^4 = C^{10}H^{11}O,C^{12}H^{11}O^3.$$

BRAZIER & GOSSLETH. (1850.) *Ann. Pharm.* 75, 254.

Produced in the preparation of caproic acid (p. 415, 3), and forms the principal part of the residue obtained in distilling crude caproic acid; rises also to the surface in the form of an oil, when the crude acid is neutralised with carbonate of potash. The oil is dried over chloride of calcium and repeatedly rectified till the boiling point remains constantly at 211°.

Bitter oil which floats on water, and boils at 211°.

| | | | Brazier & Gossleth. |
|---|---|---|---|
| 22 C | 132 | 70·97 | 70·78 |
| 22 H | 22 | 11·83 | 11·94 |
| 4 O | 32 | 17·20 | 17·28 |
| $C^{22}H^{22}O^4$ | 186 | 100·00 | 100·00 |

When boiled with alcoholic potash, it is resolved into fusel-oil and caproate of potash.

It is insoluble in water, but dissolves in all proportions in alcohol and ether. (Brazier & Gossleth.)

## Caprone.

$$C^{22}H^{22}O^2 = C^{12}H^{12}O^2,C^{10}H^{10}.$$

Brazier & Gossleth. (1850.) *Ann. Pharm.* 75, 256,

*Preparation.* The oil obtained by careful distillation of caproate of baryta (p. 417), is dried over chloride of calcium. This oil, whose boiling point rises during distillation from 120° to 170°, the greater portion however passing over between 160° and 170°, is rectified so as to obtain an oil boiling at 165°. A certain quantity of caprol $C^{12}H^{12}O^2$, a compound not yet further examined, appears however to remain mixed with the caprone, inasmuch as the analysis gives too little carbon.

*Properties.* Colourless, lighter than water, boils at 165°, and has a peculiar odour.

| | | | Brazier & Gossleth. |
|---|---|---|---|
| 22 C | 132 | 77·65 | 77·39 |
| 22 H | 22 | 12·94 | 13·14 |
| 2 O | 16 | 9·41 | 9·47 |
| $C^{22}H^{22}O^2$ | 170 | 100·00 | 100·00 |

*Decompositions.* 1. Caprone turns brown when exposed to the air. — 2. It is decomposed by strong nitric acid, even in the cold, with evolution of red vapours; the remaining liquid neutralised with carbonate of potash, yields a somewhat aromatic oil which rises to the surface; the liquid also contains a volatile acid, whose crystalline silver-salt detonates slightly when heated, and contains 42·24 p. c. silver: hence it is probably $C^{10}XH^8AgO^4$.

Caprone is insoluble in water, but soluble in *alcohol* and *ether.* (Brazier & Gossleth.)

*Appendix to Caproic Acid.*

## Vaccinic Acid.

When the butter of cow's milk is saponified, and the resulting volatile acids are saturated with baryta, there is sometimes obtained, instead of caproate and butyrate of baryta, vaccinate of baryta, a salt in which the caproic acid appears to be in some way conjugated with butyric acid (x, 80, 81).

Vaccinate of baryta crystallises in nodules of the size of walnuts, and consisting of small prisms, which dissolve into an oily liquid as readily as butyrate of baryta, and crystallise therefrom in the retort without alteration. They have a strong odour of butter, and effloresce in the air in chalky masses, which ultimately become nearly inodorous, and if then again dissolved in water, yield nothing but caproate and butyrate of baryta. The same salts are obtained from the aqueous solution of the fresh crystals, after it has been exposed for some time to the air, or continuously boiled in an open vessel; no baryta is however separated; neither does the liquid give off acid vapours, or experience any alteration of neutrality. The acid evolved from the fresh crystals by distillation with sulphuric acid, yields, when neutralised with baryta, caproate and butyrate of baryta. The aqueous solution of the fresh crystals forms with nitrate of silver, a white curdy precipitate which is quickly reduced, with brisk evolution of the odour of butyric acid. It is probably vaccinate of baryta $= C^{12}H^{11}BaO^4 + C^8H^7BaO^4 - 1\ O$. (Lerch, *Ann. Pharm.* 49, 227.)—It is perhaps $C^{20}H^{18}Ba^2O^6$, therefore still 1 At. less, according to which vaccinic acid should be regarded as a bibasic acid $= C^{20}H^{20},O^6$. (Laurent, *Compt. rend.* 25, 886.)

¶. *Oxygen-nucleus* $C^{12}H^{11}O$.

## Anhydrous Caproic Acid.

$$C^{12}H^{11}O^3 = C^{12}H^{11}O,O^2.$$

CHIOZZA. *Compt. rend.* 36, 630; *Ann. Pharm.* 86, 259.

*Caproic Anhydride, Caproic Caproate* $= (C^{12}H^{11}O^2)^2,O^2$.

Obtained by the action of oxychloride of phosphorus on caproate of baryta:

$$[3C^{12}H^{11}BaO^4 + PCl^3O^2 = 3C^{12}H^{11}O^2Cl + PBa^3O^8;$$

and:

$$C^{12}H^{11}BaO^4 + C^{12}H^{11}O^2Cl = 2C^{12}H^{11}O^3 + BaCl.]$$

The anhydrous acid is separated from the phosphate and chloride of barium by solution in ether, then digested with carbonate of soda to

remove a small portion of the hydrated acid produced at the same time, and the ether afterwards evaporated.

Colourless, mobile, oily liquid, lighter than water, and having an agreeable odour, aromatic when heated. When exposed to the air, it acquires the odour of caproic acid. (Chiozza.) ¶.

*Oxygen-nucleus* $C^{12}H^{10}O^2$.

## Pyroterebilic Acid.

$C^{12}H^{10}O^4 = C^{12}H^{10}O^2,O^2$.

Rabourdin. *N. J. Pharm.* 6, 196.

*Preparation.* Terebilic acid $C^{14}H^{10}O^8$, distilled in a retort with moderate ebullition at about 200°, gives off carbonic acid, and yields pyroterebilic acid in the form of a colourless oil, which may be freed by rectification from a small quantity of admixed terebilic acid.

*Properties.* Colourless, strongly refracting oil, of sp. gr. 1·01; boiling at a temperature above 200°. Smells somewhat like butyric acid; has a bitter, somewhat ethereal taste; produces a white spot on the tongue, and excites itching on the skin. Permanent in the air.

| | | | Rabourdin. |
|---|---|---|---|
| 12 C | 72 | 63·16 | 63·04 |
| 10 H | 10 | 8·77 | 8·78 |
| 4 O | 32 | 28·07 | 28·18 |
| $C^{12}H^{10}O^4$ | 114 | 100·00 | 100·00 |

The acid dissolves in 25 pts. of water.

In its salts, 1 At. acid is replaced by 1 At. metal; they crystallise with difficulty; their alkali-salts precipitate only the more concentrated solutions of lead or silver, and the precipitates are white.

During the washing of the lead-precipitate with water, an acid salt dissolves while a basic salt remains.

The silver precipitate is difficult to obtain in the crystalline form; it blackens on exposure to light, especially when moist.

The acid dissolves very readily in alcohol and ether. (Rabourdin.)

## Adipic Acid.

$C^{12}H^{10}O^8 = C^{12}H^{10}O^2,O^6$.

Laurent. (1837.) *Ann. Chim. Phys.* 66, 166; *Rev. Scient.* 10, 124; also *J. pr. Chem.* 27, 314; *Compt. rend.* 31, 352.
Bromeis. *Ann. Pharm.* 35, 105.
Malaguti. *N. Ann. Chim. Phys.* 16, 84.

*Preparation.* 1. From *oleic acid,* together with *lipic acid.* (x, 434.) (Laurent, Bromeis.)

2. From *tallow.* Tallow is boiled in a capacious retort with commercial nitric acid, which must be frequently renewed and the distillate poured back, till the tallow disappears and crystals separate on cooling; the liquid is then evaporated over the water-bath till it solidifies in a crystalline mass on cooling; this mass washed on a funnel, first with strong nitric acid, then with dilute nitric acid, afterwards with cold water; and the acid crystallised from its solution in boiling water by cooling and evaporation. The last crystals only appear somewhat different from the rest. (Malaguti.)

*Properties.* Mostly brownish, hemispherical, radiated nodules (soft granules, according to Bromeis), which melt at 130° (at 145°, according to Bromeis), solidify in flat needles on cooling, volatilise without decomposition (subliming in the crystalline form, according to Bromeis), and have a weaker taste than pimelic acid. (Laurent, Malaguti.)

| | | | Laurent. | Malaguti. | Bromeis. |
|---|---|---|---|---|---|
| 12 C | 72 | 49·31 | 49·94 | 48·64 | 50·25 |
| 10 H | 10 | 6·85 | 6·92 | 7·06 | 7·06 |
| 8 O | 64 | 43·84 | 43·14 | 44·30 | 42·69 |
| $C^{12}H^{10}O^{8}$ | 146 | 100·00 | 100·00 | 100·00 | 100·00 |

Metameric with oxalic ether.

According to Bromeis, it is $C^{14}H^{11}O^{9}$, which formula Laurent first adopted (*Rev. scient.* 10, 124), but afterwards rejected (*Compt. rend.* 31, 352).

*Combinations.* The acid dissolves with tolerable facility in cold, very readily in boiling *water* (Laurent); it dissolves in somewhat more than 1 pt. of water or *nitric acid.* (Bromeis.)

The *ammoniacal salt,* which crystallises in needles, does not precipitate the salts of baryta, strontia, lime, magnesia, manganous oxide, cadmic oxide, lead oxide, cupric oxide, or nickel oxide. (Laurent, Bromeis.)

*Baryta-salt.* — Contains, in the dry state, 54·3 p. c. baryta (Laurent); 51·51 p. c. baryta. (Bromeis.)

*Strontia-salt.* — From a mixture of the ammonia-salt with chloride of strontium, alcohol throws down microscopic needles which, at 130° in vacuo, give off 9·2 p. c. (nearly 3 At.) water. (Laurent.)

*Lime-salt.* — Prepared in a similar manner in vacuo. The precipitate gives off 8·4 p. c. water at 100°.

| *Crystals.* | | | Laurent. |
|---|---|---|---|
| $C^{12}H^{8}O^{6}$ | 128 | 63·37 | |
| 2 CuO | 56 | 27·72 | 25·74 |
| 2 HO | 18 | 8·91 | 8·40 |
| $C^{12}H^{8}Cu^{2}O^{8} + 2Aq$ | 202 | 100·00 | |

*Lead-salt.* — Contains 60·5 p. c. lead-oxide. (Laurent.)

The *Ammonia-salt* forms a pale brick-red precipitate with hydrochlorate of ferric oxide. (Laurent.)

*Silver-salt.* — The ammonia-salt forms, with not too small a quantity of nitrate of silver, a precipitate (Bromeis), which is white. (Laurent.)

| | | | | Bromeis. | Laurent. |
|---|---|---|---|---|---|
| 12 C | 72 | .... | 20·00 | ........ 22·50 | |
| 8 H | 8 | .... | 2·22 | ........ 2·64 | |
| 2 Ag | 216 | .... | 60·00 | ........ 56·41 | .... 57·00 |
| 8 O | 64 | .... | 17·78 | ........ 18·45 | |
| $C^{12}H^8Ag^2O^8$ | 360 | .... | 100·00 | ........ 100·00 | |

According to Bromeis, the formula is $C^{14}H^9Ag^2O^9$; it is to be suspected however that the acid and its salts were examined in different degrees of purity.

The acid dissolves very readily in hot *alcohol* and *ether*. (Laurent.)

The acid which Laur. Smith (*Ann. Pharm.* 42, 252) obtained by treating spermaceti with nitric acid, containing 50·2 p. c. C, 7·0 N and 42·8 O, and whose silver-salt contains 22·58 p. c. C, 2·68 H, and 55·98 Ag., belongs perhaps to this place.

*Conjugated Compound.*

## Adipate of Ethyl.

$$C^{20}H^{18}O^8 = 2C^4H^5O,C^{12}H^8O^6.$$

Malaguti. (1846.) *N. Ann. Chim. Phys.* 16, 85.

*Adipic ether.*

The alcoholic solution of adipic acid is saturated with hydrochloric acid gas, &c. &c.

Yellowish oil of sp. gr. 1·001 at 20·5°, boiling with decomposition at 230°, having a strong odour of apples and a bitter caustic taste.

Chlorine gas acts strongly on the ether, hydrochloric acid being cooled, and the liquid quickly thickening into a mass of the consistence of turpentine. (Malaguti.)

| | | | | Malaguti. |
|---|---|---|---|---|
| 20 C | 120 | .... | 59·41 | ........ 59·29 |
| 18 H | 18 | .... | 8·91 | ........ 9·06 |
| 8 O | 64 | .... | 31·68 | ........ 31·65 |
| $C^{20}H^{18}O^2$ | 202 | .... | 100·00 | ........ 100·00 |

*Oxygen-nucleus* $C^{12}H^8O^4$.

## Terechrysic Acid.

$$C^{12}H^8O^{10} = C^{12}H^8O^4,O^6.$$

Caillot. (1847.) *N. Ann Chim. Phys.* 21, 27; also *J. pr. Chem.* 42, 233.

*Preparation.* A small quantity of oil of turpentine is distilled with a large quantity of nitric acid diluted with an equal quantity of water, as long as red fumes continue to escape; the liquid decanted from the resulting resin and evaporated; the residue dissolved in cold water; and the solution decanted, evaporated, and left at rest,— whereupon it deposits, first crystals of oxalic acid, then a greyish white sediment consisting of oxalic, terebic, terephthalic, and terebinzic acids, and yields a mother-liquor containing terechrysic acid, together with the acids just mentioned, dissolved in a small quantity of nitric acid. This mother-liquor is evaporated to the consistence of honey, during which process the rest of the oxalic acid is completely [?] destroyed by the remaining nitric acid; the syrup redissolved in a small quantity of water; the solution separated from the sparingly soluble terebinzic acid neutralised with carbonate of baryta, filtered from the terebinzate and terephthalate of baryta, and precipitated by sulphuric acid; and the filtrate, which, together with terechrysic acid, contains also small quantities of nitric and terebic acids, poured into boiling aqueous acetate of lead. The liquid on cooling then deposits slender crystals of terechrysate of lead, which may be decomposed by dilute sulphuric acid.

*Properties.* As obtained by evaporation of the aqueous solution, it is an orange-yellow, amorphous, non-volatile paste, having a strongly acid taste, with rough and bitter after-taste.

It yields by dry distillation, first carbonic acid, and a small quantity of coloured acid distillate, then combustible gases, a yellowish oil, and a large quantity of compact charcoal.

It dissolves in all proportions in *water.*

Its salts are yellow or aurora-red, and mostly soluble in water.

| *Lead-salt at* 120. | | | Caillot. a. | b. |
|---|---|---|---|---|
| 12 C | 72 | 19·67 | 18·15 | 18·88 |
| 6 H | 6 | 1·64 | 1·57 | 1·72 |
| 2 PbO | 224 | 61·20 | 60·77 | 62·10 |
| 8 O | 64 | 17·49 | 19·51 | 17·30 |
| $C^{12}H^6Pb^2O^8$ | 366 | 100·00 | 100·00 | 100·00 |

Salt *b* is salt *a* freed from admixed terebinzate of lead by repeated boiling with water.

The acid dissolves in all proportions in *alcohol* and *ether.*

*Terechrysate of Ethyl* is a dark, yellowish red, gummy liquid, which yields, by dry distillation, a nearly colourless, ethereal distillate, together with oil and a large quantity of charcoal. (Caillot.)

*Amidogen-nucleus* $C^{12}AdH^{11}$.

## Leucin.

$C^{12}NH^{13}O^4 = C^{12}AdH^{11},O^4$.

PROUST. *Ann. Chim. Phys.* 10, 40; also *N. Tr.* 4, 1, 221.

BRACONNOT. *Ann. Chim. Phys.* 13, 119; also *Schw.* 29, 349; also *Gilb.* 70, 396,— *Ann. Chim. Phys.* 35, 161; also *N. Tr.* 18, 1, 270.

MULDER. *J. pr. Chem.* 16, 290; abstr. *Ann. Pharm.* 28, 79; *J. pr. Chem.* 17, 57.
BOPP. *Ann. Pharm.* 69, 20.
LAURENT & GERHARDT. *N. Ann. Chim. Phys.* 24, 321; also *N. J. Pharm.* 14, 311.
CAHOURS. *Compt. rend.* 27, 265; also *J. pr. Chem.* 45, 350.
LIMPRICHT. *Ann. Pharm.* 94, 243.
GÖSSMANN. *Ann. Pharm.* 90, 184; 91, 129.
STRECKER. *Ann. Pharm.* 68, 54.

*Aposepedin, Käsoxyd, Oxyde caséeux.* — Proust, in 1818, discovered caseous oxide as a product of the putrefaction of cheese; and Braconnot in 1820 found it among the products of decomposition of animal substances by oil of vitriol. Mulder, in 1838, showed that the two substances are identical.

*Sources.* — In old cheese. (Proust.) Probably the substance found by Laissaigne & Collard in the black vomit, and called caseous acid, is nothing but leucin. In fresh calf's liver (Liebig, *Chem. Briefe*, 3 Aufl. 453); also, together with tyrosin in the human liver, in certain cases of disease, but not in the healthy liver. (Frerichs & Städeler. *Archiv. f. Physiologie*, 1854, 382.) According to later researches by these chemists (*Verhandl. d. naturf. Gesellsch*, in *Zurich*, Joli, 1855), leucin and tyrosin are very widely diffused in the animal organism. Leucin also exists, together with taurin, inosite and uric acid, in the tissue of the lungs. (A. Cloëtta, *Ann. Pharm.* 92, 289.) — According to Gorup-Besanez (*Ann. Pharm.* 98, 7), leucin occurs in many parts of the glandular system, viz., in the thymoïd and thyroïd glands, in the liver, and especially in the pancreas.

*Formation.* 1. In the decomposition of gelatin, muscular flesh, legumin or wool, (or white of egg, according to Mulder,) by oil of vitriol (Braconnot); together with a small quantity of glycocol. (Mulder.) — 2. By heating horn with dilute sulphuric acid (Hinterberger); also, together with tyrosin, by heating elastic tissue, especially the neck-band (Zollikofer), or feathers, hedge-hogs' spines, human hair, the wing-cases of cockchafers, or globulin and hæmatin from ox-blood (Leyer & Köller, *Ann. Pharm.* 83, 332), or silk (Hinterberger, *Wien. Akad. Ber.* 11, 450) with dilute sulphuric acid. — 3. By boiling white of egg, gelatin, or flesh, with potash-ley, glycocol being formed at the same time. (Mulder.) Hence also, when the juice of mangold-wurzel is boiled with lime. (Hochstetter, *J. pr. Chem.* 29, 36.) — 4. By fusing albumin, fibrin, casein (Bopp), or horn (Hinterberger), with hydrate of potash. — 5. In the putrefaction of casein or gluten under water (Proust, Mulder); sometimes abundantly, sometimes only in traces. (Cahours.) ¶. Also, together with tyrosin, ammonia, butyric acid, and lactic acid, by the putrefaction of yeast. (A. Müller, *J. pr. Chem.* 57, 162, 447.) — By the action of oxide of silver and water on thialdin. (Gössmann.)

$$[\underbrace{C^{12}NH^{13}S^4}_{\text{thialdin.}} + 4AgO = C^{12}NH^{13}O^4 + 4AgS.]$$

6. By the action of hydrocyanic acid and dilute hydrochloric acid, with the aid of heat, on valeral-ammonia. (Limpricht, Parkinson; see page 20.)

$$NH^3,C^{10}H^{10}O^2 + C^2NH + HCl + 2HO = C^{12}NH^{13}O^4 + NH^4Cl.$$ ¶.

*Preparation.* 1. Finely-chopped beef, washed with water and then strongly pressed, is mixed with an equal weight of oil of vitriol, and gently heated till it is completely dissolved; the fat skimmed off after cooling; the mixture diluted with water amounting to $3\frac{1}{2}$ times the weight of the meat; the liquid boiled for 9 hours with frequent renewal of the water; the sulphuric acid removed by chalk; the filtrate evaporated to an extract; this extract repeatedly boiled with alcohol of 34° Bm.; the resulting alcoholic tincture evaporated; the dry residue exhausted with cold alcohol; the residual mixture of leucin and a small quantity of matter precipitable by tannin dissolved in water; a solution of tannin carefully added to it by drops as long as any precipitate ensues; and the liquid filtered after a few seconds, then evaporated. (Braconnot.) — The leucin prepared by Braconnot appears still to have contained glycocol. (Mulder.)

2. One part of dry albumin, fibrin, or casein, free from fat, is boiled with 4 pts. of oil of vitriol and 12 pts. of water, in an open vessel, the ebullition being continued for a day and the water continually renewed. Or, better: 1 pt. of the substance is dissolved in 4 pts. of strong hydrochloric acid; the liquid mixed with 3 or 4 pts. of oil of vitriol and evaporated over the water-bath till the greater part of the hydrochloric acid is expelled; and the remaining black-brown pitchy or syrupy mass, in which minute crystals form, dissolved in hot water. — Either of these acid liquids is boiled with excess of milk of lime to expel ammonia, then strained through a linen bag; the clear filtrate treated with sulphuric acid to precipitate the lime which is held in solution by a product of decomposition; the excess of acid precipitated by acetate of lead, and the excess of lead by sulphuretted hydrogen; and the filtrate evaporated to a syrup, from which in a few days leucin and tyrosin crystallise. The crystals are freed from the syrupy mother-liquor by digestion in 86 per cent. alcohol, and the leucin separated from the tyrosin and brown matter by treatment with water, hydrated oxide of lead, and animal charcoal, as in the 5th mode of preparation. — The mother-liquor dissolved in alcohol and set aside for two months, still yields crystals consisting of a large quantity of leucin and a small quantity of a peculiar substance less soluble in water. — This substance, when purified, forms dull white needles, and sublimes like leucin, without residue, in flocks resembling cotton, but is sparingly soluble in water, almost insoluble in hydrochloric acid or in potash, easily soluble in absolute alcohol. (Bopp.)

3. One pt. of cow-horn shavings is boiled with 4 pts. of oil of vitriol and 12 pts. of water for 36 hours, the water being renewed from time to time; the liquid then supersaturated with milk of lime; the whole boiled for 24 hours in an iron pot, then strained through a conical bag and squeezed, and the liquid mixed with a very slight excess of sulphuric acid, filtered, and evaporated: it then yields at first, spherical crystalline masses of tyrosin, and afterwards laminated masses of leucin. The latter are pressed between paper, freed from brown matter by washing with absolute alcohol, and crystallised from solution in a small quantity of hot water, tyrosin then separating first, and the mother-liquor afterwards yielding leucin, tolerably pure but not quite white. It must therefore be dissolved in hot water; digested with a small quantity of hydrated oxide of lead; filtered; the filtrate freed from lead by sulphuretted hydrogen; and the

crystallised leucin further treated with animal charcoal. (Hinterberger, *Ann. Pharm.* 71, 72.)

4. White of egg, gelatin, or flesh, is boiled with potash-ley till it is completely decomposed; the liquid neutralised with sulphuric acid, and evaporated; and the leucin extracted with alcohol. (Mulder.)

5. One pt. of the powder of dry albumin, fibrin, or casein free from fat, is added to 1 pt. of hydrate of potash heated to fusion in an iron crucible of 25 times the capacity; and water carefully added after half an hour, when the violent frothing arising from the escape of water and ammonia has subsided, and the brown colour which the mixture at first exhibits, is changed to yellow: if the liquid be then saturated with acetic acid, filtered hot, and gradually cooled, it yields tufts of needles consisting of tyrosin. These crystals completely fill the filtrate, when the process is well conducted; on the other hand, they are less abundant the longer the fusion has been continued. — The liquid decanted from the crystals of tyrosin is evaporated till a crystalline film appears on the surface; then set aside for 24 hours and exhausted with strong alcohol, which leaves crystals of leucin and the still remaining tyrosin; the liquid mixed with alcoholic sulphuric acid, and decanted from the crystallised sulphate of potash; the alcohol separated from it by evaporation, the sulphuric acid by lead, and then the lead by sulphuretted hydrogen; and the solution finally evaporated, whereupon it yields crystals of leucin, and a greasy syrup, the quantity of which is less in proportion as the fusion has been longer continued. — To purify the leucin from tyrosin and a small quantity of brown colouring matter, it is disolved in such a quantity of hot water that only a small quantity of leucin may separate on cooling, together with the tyrosin; the mother-liquor digested with hydrated oxide of lead, which removes the colouring matter together with a small quantity of leucin; the filtrate treated with sulphuretted hydrogen; and the filtrate then obtained, which has merely a yellowish colour, evaporated in a flask till a crystalline film forms on its surface. It then, on cooling, yields crystals of leucin, which must be washed with cold water and alcohol, and decolorised by treatment with animal charcoal and recrystallisation. — If the object be merely to obtain leucin, and not tyrosin, it is sufficient to heat the potash mixture till the strongest intumescence is over. At that stage of the process, the same quantity of leucin is formed, but no tyrosin. (Bopp.)

6. Moist gluten or casein precipitated by acetic acid is left to putrefy at about 10° under water, which is from time to time poured off and renewed, so that the putrefaction may not be interrupted by the accumulation of phosphate, acetate, and caseate [lactate?] of ammonia; the decanted liquid evaporated to a syrup, which in a few days solidifies into a red saline mass having a sharp disagreeable taste; this mass washed with cold alcohol, which extracts the salts, till the taste of cheese is removed; the residual white powder washed with water; the hot filtrate evaporated till a crust forms on it; and this crust, after cooling, freed from the still saline mother-liquor by decantation and washing with cold water. (Proust.) The product still requires to be freed from adhering fat by repeated solution in boiling water and treatment with animal charcoal.

7. One pt. of cheese, muscular flesh, or white of egg, is left to putrefy with 50 pts. of water for 6 weeks at a temperature somewhat above 20°, the resulting turbid solution boiled with a small quantity of milk of lime; the lime precipitated by a very slight excess of sulphuric acid; the filtrate

boiled down and precipitated by neutral acetate of lead; the decanted liquid treated with sulphuretted hydrogen; the filtrate evaporated to a syrup; and the leucin which crystallises therefrom, freed from the remaining syrup by means of alcohol, and purified by solution in water, treatment with hydrated oxide of lead and sulphuretted hydrogen, crystallisation, washing with cold water and alcohol. — When the above-mentioned alcoholic solution of the syrup is evaporated to complete dryness, and the residue dissolved in absolute alcohol, the solution still deposits a small quantity of leucin. (Bopp.)

¶. 8. The neck-band of the ox, after being freed from the surrounding fibrous tissue by boiling with water containing acetic acid and subsequent scraping with a knife, and (if necessary) from fat by digestion in ether, is boiled for 48 or 50 hours with dilute sulphuric acid (8 pts. oil of vitriol to 12 pts. water), the water being replaced as it evaporates. The resulting solution is mixed with a slight excess of thin milk of lime, and boiled for some hours; the filtrate exactly neutralised with sulphuric acid and evaporated; and the liquid, after filtration from the separated sulphate of lime, exactly neutralised with sulphuric acid and evaporated. It then yields, especially on cooling, impure leucin, which may be purified by recrystallisation from hot alcohol. This process is peculiarly advantageous, the acid mother-liquors crystallised to the last drop, yielding nothing but leucin. (Zollikofer, *Ann. Pharm.* 82, 162; *compare* Gossmann. *Ann. Pharm.* 91, 130.)

9. Thialdin is enclosed, together with oxide of silver and water, in a glass tube, and heated for three or four hours in boiling water; the liquid then filtered from the sulphide of silver, and evaporated to a syrup. It then gradually solidifies into a crystalline mass of leucin, which may be purified by crystallisation from boiling absolute alcohol. — Oxide of lead may also be used, but does not give so good a result. (Gössman.)

10. Valeral-ammonia is boiled in a retort with hydrocyanic and hydrochloric acids till the oily layer, consisting of the fused ammonia-compound, has completely disappeared; the solution then left to itself till the greater part of the resulting chloride of ammonium has crystallised out; the hydrochloric acid removed by means of hydrated oxide of lead, and the lead by sulphuretted hydrogen; the filtrate evaporated over the water-bath, and the residue dissolved in hot dilute alcohol: the solution thus obtained yields crystals of pure leucin. (Limpricht.) ¶.

*Properties.* White soft mass, resembling cholesterin, floating on water, unctuous to the touch. (Proust.) Dendrites, or nodules and rings made up of soft silky needles, grating between the teeth, easily pulverised, inodorous, having a slightly bitter taste like roast meat or broth. (Braconnot.) White crystalline powder. (Gössmann.) Crystallises from alcohol in nacreous scales resembling cholesterin; soft to the touch, and floating on water. (Mulder.) When heated in a tube open at both ends, it sublimes, almost wholly undecomposed, in soft extended ramifications. (Braconnot.) Sublimes completely at 170°, without fusion or decomposition (Mulder), in cotton-like flocks (Bopp), diffusing itself in the air like oxide of zinc. (Hinterberger.)

| | | | Mulder. | Cahours, *acc. to* (1). | Cahours, *acc. to* (6). | Strecker. |
|---|---|---|---|---|---|---|
| 12 C | 72 | 54·96 | 55·59 | 54·96 | 55·05 | 54·55 |
| N | 14 | 10·69 | 10·51 | 10·89 | 10·74 | |
| 13 H | 13 | 9·92 | 9·26 | 10·05 | 9·38 | 10·09 |
| 4 O | 32 | 24·43 | 24·64 | 24·10 | 24·83 | |
| $C^{12}NH^{13}O^{4}$ | 131 | 100·00 | 100·00 | 100·00 | 100·00 | |

| | Laurent & Gerhardt. | Zollikofer, *a.* | *b.* | *c.* | Limpricht, *acc. to* (10). |
|---|---|---|---|---|---|
| C | 54·6 | 54·67 | 53·56 | | 54·9 |
| N | | 10·92 | | | |
| H | 9·9 | 10·06 | 10·42 | 10·69 | 10·0 |
| O | | 24·35 | | | |
| | | 100·00 | | | |

Leucin does not give off any water at 108°, not even when mixed with oxide of lead (Mulder).—Laskowski's analysis also agrees with the above formula, first proposed by Laurent & Gerhardt (*Ann. Pharm.* 68, 364). Zollikofer's analysis *a* was made with a purer product than *b* or *c*.—Leucin is homologous with glycocol $C^4NH^5O^4$, and sarcosin $C^6NH^7O^4$ (Laurent & Gerhardt).—Braconnot & Liebig (*Ann. Pharm.* 57, 134) supposed leucin to contain sulphur.

*Decompositions.* 1. When leucin (6) is distilled at a gentle heat, a large portion of it sublimes undecomposed, and the remainder is resolved into a small quantity of water, ammonia, and very light charcoal, and a large quantity of yellow oil which has a fatty and alliaceous odour, and solidifies on cooling. (Proust.) Leucin (6) heated [somewhat strongly?] in a retort melts, swells up, does not yield any sublimate, but gives off, first an aqueous solution of carbonate and hydrosulphate of ammonia, and afterwards a large quantity of matter having the consistence of tallow. (Braconnot.) Leucin (1) melts at a temperature above 100°, emitting the odour of roast meat, and partly sublimes in white granular crystals; while the remainder is resolved into an ammoniacal and empyreumatic oily distillate. (Braconnot.) Leucin (8) when cautiously heated volatilises in thick white fumes, without previous fusion; when more rapidly heated, it melts and leaves a carbonaceous residue. (Gösmann.) 2. Leucin *burns* readily, and with a white flame in contact with the air. (Proust, Braconnot.)

3. Leucin is decomposed by *chlorine*, forming a brown hard body, similar to that obtained with glycocol (ix, 250), and a red volatile liquid. Mulder.) — 4. When heated for some time with a sufficient quantity of *nitric acid*, it is completely resolved into gases, but so long as the decomposition is incomplete, the still remaining portion exhibits the characters of nitroleucic acid. (Mulder.) Leucin (6) dissolves in nitric acid, and the solution when heated, gives off gases, and is quickly converted into oxalic acid and a very small quantity of a substance resembling picric acid. (Proust.) Its solution in nitric acid evaporated to the consistence of honey and diffused in a small quantity of water, is resolved into a yellow oil, and a yellow, bitter, rough-tasting liquid, containing ammonia and sulphuric acid [?], but no oxalic acid. (Braconnot.) — ¶. 5. When nitric oxide is passed into a solution of leucin in nitric acid, nitrogen is evolved, and *leucic acid* $C^{12}H^6O^6$ is formed. (Strecker, *Ann. Pharm.* 68, 55.)

$$[C^{12}NH^{13}O^4 + 3O = C^{12}H^{12}O^6 + HO + N.]$$

This acid is oily, dissolves very readily in ether, and forms with baryta a salt which crystallises in laminæ. The same acid is formed when chlorine is passed, not in excess, into a dilute solution of caustic soda. (Gössmann.) — 6. Chlorine gas passed to saturation into a solution of leucin in carbonate of potash, forms chloride of cyanogen, valerianic acid, and valeronitril. (Gössmann.) ¶. — 7. Leucin distilled with *peroxide of manganese* and dilute *sulphuric acid* yields valeronitril and carbonic acid:

$$C^{12}NH^{13}O^4 + 4O = C^{10}NH^9 + 2CO^2 + 4HO.$$

When stronger sulphuric acid is used, valerianic acid passes over, and the residue contains ammonia. When leucin is distilled merely with *peroxide of lead* and water, only a trace of valeronitrile passes over, but a large quantity of butyral and then ammonia, which crystallise together in the form of butyral-ammonia. — 8. Leucin, freed with *hydrate* of *potash*, gives off ammonia and hydrogen and forms valerate of potash. (Liebig, *Ann. Pharm.* 57, 127.) — 9. An aqueous solution of leucin emits a very offensive odour and forms a peculiar acid, perhaps $C^{12}H^{12}O^6$. (Cahours.) — In vacuo, the aqueous solution of leucin appears to remain undecomposed. (Gössmann). — 10. When a solution of 1 part of leucin in water, is set aside for some weeks in contact with a quantity of moist fibrin, which in the dry state would weigh $\frac{1}{2}$ pt., putrefaction takes place, the greater part of the leucin is decomposed, and ammonia is produced, together with such a quantity of valerianic acid as cannot be wholly produced from the fibrin. (Bopp.)

*Combinations.* Leucin dissolves sparingly in cold *water*, by which it is not wetted, but readily in water of 60° (Proust); it dissolves in 14 pts. of 22° (Braconnot); in 27·7 pts. of cold water. (Mulder.)

Its solution in *oil of vitriol* does not become coloured when heated. (Mulder.)

It dissolves readily in *hydrochloric acid* (more readily than in water, according to Braconnot) and in *dilute sulphuric acid*, and the solution may be evaporated at 100° without decomposition, (Bopp.) The evaporated hydrochloric solution solidifies every time it is cooled. (Braconnot.) The crystals of hydrochlorate of leucin contain 20·6 p. c. Cl, and are therefore $C^{12}NH^{13}O^4,HCl$. (Laurent & Gerhardt.) Leucin likewise absorbs 27·93 p. c. (1 At.) of hydrochloric acid gas. (Mulder.)

It dissolves readily in *nitric acid*, forming *Nitroleucic acid*, which separates out by evaporation and cooling, as a crystalline mass; and by pressing this mass between paper, and recrystallising, the acid is obtained in tufts of colourless needles, having a more acid taste than nitroglycolic acid. (Braconnot.) Leucin dissolves without effervescence in cold nitric acid not in excess, and the solution soon solidifies in crystalline grains which change to needles by recrystallisation. The slight effervescence which takes place in the solution of the leucin, probably arises from a small quantity of carbonate of ammonia. (Laurent & Gerhardt.)

| *Needles at* 100°. | | | Mulder. | Laurent & Gerhardt. |
|---|---|---|---|---|
| 12 C | 72 | 37·11 | 38·03 | 36·9 |
| 2 N | 28 | 14·43 | | |
| 14 H | 14 | 7·22 | 6·87 | 7·2 |
| 10 O | 80 | 41·24 | | |
| $C^{12}NH^{13}O^4,HO,NO^5$ | 194 | 100·00 | | |

Leucin dissolves readily in aqueous potash, but without neutralising it. (Proust.)

*Nitroleucate of baryta* contains 41·01 p. c. baryta. (Mulder.) — *Nitroleucate of lime* crystallises in roundish groups, melts in its water of crystallisation when thrown on red-hot coals, and then deflagrates, but less quickly than nitroglycolate of lime. — The *magnesia-salt* forms small granular crystals which do not become moist. (Braconnot.) — With *nitrate of silver* also leucin forms a crystallisable salt. These salts have doubtless the formula $C^{12}NH^{13}O^4, MO, NO^5$. (Laurent & Gerhardt.)

*Leucin with Oxide of Lead.* — An aqueous solution of leucin forms a white precipitate with basic acetate of lead. (Braconnot.) — A boiling aqueous mixture of leucin and neutral acetate of lead, deposits, on careful addition of ammonia, nacreous laminæ, which contain 29·3 p. c. C and 46·3 PbO, and are therefore $PbO,C^{12}NH^{13}O^4$. (Strecker, *Ann. Pharm.* 72, 89.) — ¶ Gössmann obtained a salt of the same composition; but in one experiment, possibly in consequence of a peculiar degree of concentration, he obtained, not immediately on boiling, but after the solution had been left for some time in a close vessel, laminated groups of crystals of tolerable size, resembling lithia-mica. These crystals had a green lustre, became yellow and afterwards red-brown when heated, without essential alteration of form, and afterwards gave off a very small quantity of leucin-vapour. Before ignition, they withstood for a long time the action of strong sulphuric acid; but when ignited, with addition of nitric and sulphuric acid, they left 119·2 p. c. sulphate of lead: therefore $9PbO,C^{12}NH^{13}O^4$.

*Leucin with Cupric oxide.* — Recently precipitated cupric oxide dissolves readily in aqueous leucin, forming a bluish liquid, which on cooling deposits crystalline grains or laminæ having the colour of ammoniacal sulphate of copper. (Gössmann.)

| | | | Gössmann. |
|---|---|---|---|
| 12 C | 72 | 42·11 | 41·33 |
| N | 14 | 8·19 | |
| 13 H | 13 | 7·60 | 6·69 |
| 4 O | 32 | 18·71 | |
| CuO | 40 | 23·39 | 22·8 |
| $CuO,C^{12}NH^{13}O^4$ | 171 | 100·00 | |

Aqueous leucin boiled with excess of *cupric hydrate,* yields an insoluble compound. When cupric sulphate is added to an aqueous solution of leucin, the liquid assumes a darker colour, and does not become turbid, even at the boiling heat, on addition of a quantity of potash equivalent to that of the sulphuric acid contained in the liquid. (Gössman.) ¶.

Aqueous leucin added to a solution of *mercurous nitrate* throws down an abundance of white flakes, the supernatant liquid acquiring a red colour. (Braconnot.)

¶ *Leucin with Mercuric oxide.* — Recently precipitated mercuric oxide dissolves very readily and in considerable quantity in aqueous leucin; and the solution, when evaporated, deposits, first crystalline granules, and afterwards laminæ containing 47·3 p. c. mercuric oxide: therefore $HgO,C^{12}NH^{13}O^4$. (Gössmann.)

Aqueous leucin is not precipitated by mercuric nitrate or chloride; but on addition of potash or ammonia, a white bulky precipitate is formed, which dissolves in excess of potash: the precipitate gradually becomes gelatinous and decomposes during washing. (Gössmann.) According to R. Hoffmann, on the contrary (*Ann. Pharm.* 87, 123), pure leucin is precipitated by mercuric nitrate in white flakes, without red colouring of the supernatant liquid, the production of such a colour indicating the presence of tyrosin ¶.

Leucin dissolves in 658 pts. of cold alcohol of sp. gr. 0·828; its hot solution becomes turbid on cooling. (Mulder.) Leucin (6) dissolves very sparingly in boiling alcohol, and yields on cooling, crystalline granules (Proust), a soft powder. (Braconnot.) Leucin (1) dissolves to a sensible amount only in heated alcohol. (Braconnot.) Leucin dissolves sparingly in ordinary, and very sparingly in absolute alcohol. (Bopp). — Leucin is likewise insoluble in warm ether. (Proust, Mulder.)

*Acetic acid* or *acetate of potash* increases the solubility of leucin in water or alcohol. (Bopp). — According to Braconnot, leucin (1) is not precipitated by *tannin*, but leucin (6) produces with infusion of galls, white flocks which dissolve in excess of the infusion; further examination is therefore required to determine the real nature of the reaction.

*Oxyamidazo-nucleus* $C^{12}NAdH^4O^6$.

## Amalic Acid.

$$C^{12}N^2H^6O^8 = C^{12}NAdH^4O^6,O^2.$$

Rochleder. (1849). *Ann. Pharm.* 71, 1.— *Wien. Akad. Ber. d. Wiss.* 1850, 2, 98.

From αμαλις, because it is slightly acid and has but little solidity.

*Preparation.* Chlorine gas is passed through caffeine or theobromine made into a paste with water, till the liquid no longer becomes heated, and when placed under the microscope, no longer exhibits a separation of slender needles on being mixed with potash. The liquid is then evaporated over the water-bath, as long as the crystals increase; and these crystals are collected after cooling, washed with cold water, boiled with absolute alcohol, and crystallised from boiling water.

*Properties.* Colourless, rather large, soft crystals, deceptively like alloxantin, which melt by heat, do not give off any water at 100°, redden litmus very slightly, and are reddened by ammonia; their solution imparts to the skin, after a while, a red colour and offensive odour, like aqueous alloxan.

| | | | Rochleder. |
|---|---|---|---|
| 12 C | 72 | 42·35 | 41·97 |
| 2 N | 28 | 16·47 | 16·46 |
| 6 H | 6 | 3·53 | 4·24 |
| 8 O | 64 | 37·65 | 37·33 |
| $C^{12}N^2H^6O^8$ | 170 | 100·00 | 100·00 |

It is distinguished from alloxan (x, 171) by the addition of $C^4H^4$.—According to Rochleder, it is $C^{12}N^2H^7O^8$.

*Decompositions.* 1. The acid heated above its melting point, turns first yellow, then reddish-yellow, then brown (dissolving at that point with purple-red colour in water); gives off ammonia, an oil, and a crystalline

body; and leaves a trace of charcoal. — 2. By chlorine, it is converted into nitrothein (x, 483):

$$[C^{12}N^2H^6O^8 + 2Cl + 2HO = C^{10}N^2H^6O^6 + 2CO^2 + 2HCl.]$$

3. With hot nitric acid, it gives off red vapours and forms peculiar crystals. — 4. From silver salts it reduces the metal in black flocks. — 5. By ammonia, it is converted into a dark red body, *Murexoin*. Hence in contact with air (containing ammonia), it assumes a rose-red, then a violet and ultimately a brown-red colour. When the acid slightly moistened is spread upon a dish, and exposed under a bell-jar to air in which ammoniacal gas is diffused by the presence of aqueous ammonia, then pressed between paper after it has acquired the brown-red colour, and dissolved in water at 90°, or in warm alcohol, it yields murexoin in scarlet four-sided prisms, which reflect light with golden-yellow colour from two of their faces, assume a golden lustre under the burnisher, do not give off any thing at 100° in vacuo, and in this state contain 43·30 p. c. C, 27·50 N, 5·09 H, and 24·11 O: therefore = $C^{36}N^5H^{23}O^{15}$ [?]; when heated, they partly volatilise undecomposed in violet vapours. The purple-red aqueous solution is not coloured violet by potash, but immediately decolorised. [If murexoin were = $C^{24}N^6H^{16}O^{12}$, it would differ from the similar body murexide (x, 192) only by containing $C^8H^8$ more]. — 6. With potash, soda, and baryta, amalic acid forms dark red compounds, which are tolerably stable when they contain excess of acid, but are decolorised when they contain more alkali, baryta then producing in the hot solution, a white gelatinous precipitate. — 7. With ferrous salts mixed with alkali, the aqueous acid forms a dark indigo-coloured precipitate. (Rochleder). — ¶ 8. The acid heated with a concentrated solution of bisulphite of ammonia, yields a pale yellow solution, which becomes darker yellow at the boiling heat, but in a few minutes loses its colour, and solidifies in a pasty mass, in consequence of the formation of white, silky, needle-shaped crystals, consisting of the compound $C^{20}N^4H^{14}O^{11}$. This compound, in the moist state, soon acquires a rose-red colour by the action of the ammonia in the air. It is decomposed by heat, giving off a vapour which is partly colourless, partly purple. It dissolves readily in acids, but with difficulty or not at all, in other solvents. Its solution in hydrochloric acid does not precipitate bichloride of platinum, either alone, or on addition of alcohol or ether. The aqueous mixture of the two salts, decomposes however after some time, depositing a platinum-compound in light yellow crystals insoluble in alcohol and containing 58·77 p. c. platinum, which corresponds very nearly with Reiset's compound $N^2H^6PtCl$. (Rochleder & Schwarz, *Wien. Akad. d. Wiss.* 12, 190; *J. pr. chem.* 63, 129) ¶.

*Combinations.* Amalic acid is insoluble in cold, sparingly soluble in hot *water*, and separates from the solution in flocks when cooled with agitation, but in larger crystals, when the solution is left at rest for some hours.

It dissolves sparingly in boiling absolute alcohol. (Rochleder).

*Primary-nucleus* $C^{12}H^{14}$.

*Oxygen-nucleus* $C^{12}H^{8}O^{6}$.

## Lactide.

$$C^{12}H^{8}O^{8} = C^{12}H^{8}O^{6},O^{2}.$$

JUL. GAY-LUSSAC & PELOUZE. (1833). *Ann. Chim. Phys.* 52, 410; also *Ann. Pharm.* 7, 43.
CORRIOL. *J. Pharm.* 19, 373. — *J. Scienc. Phys.* 3, 421.
PELOUZE. *N. Ann. Chim. Phys.* 13, 260; also *Ann. Pharm.* 53, 116.
ENGELHARDT. *Ann. Pharm.* 70, 243.

*Sublimed Lactic acid, Anhydrous Lactic acid.*

*Formation.* By the dry distillation of lactic acid or rather of lactic anhydride (p. 479).

*Preparation.* The buttery, white, bitter, acid sublimate obtained by the dry distillation of lactic acid, is pressed between paper and crystallised from boiling alcohol (Gay-Lussac & Pelouze), or from ether according to Corriol.— 2. The entire distillate obtained by distilling lactic anhydride between 250° and 260°, is freed from aldehyde by heating it to 100°; and the residue, which solidifies on cooling into a brownish crystalline pulp, is washed on a filter with cold absolute alcohol (which dissolves ordinary lactic acid and citraconic acid) till it is decolorised, and left to crystallise from solution in the smallest possible quantity of absolute alcohol. The lactide which remains in the mother-liquor is lost as such, inasmuch as it is converted during the evaporation, into ordinary lactic acid. (Engelhardt.)

White rhombic tables. (Gay-Lussac & Pelouze.) Large crystals, apparently belonging to the oblique prismatic system, having the habit of green vitriol, and breaking to pieces on drying. (Engelhardt.) Melts at 107° (Gay-Lussac & Pelouze), above 100°, and afterwards solidifies in the crystalline state at 74°. (Corriol.) Boils without decomposition at 250°, giving off white pungent vapours (Gay-Lussac & Pelouze), and when not too strongly heated, may be sublimed without decomposition. (Corriol.) Sinters together at 120°, subliming at the same time very slowly, and fuses only at a higher temperature, at which also it sublimes more quickly. (Engelhardt.) Inodorous: tastes less sour than lactic acid. (Gay-Lussac & Pelouze.) It is tasteless at first, but soon takes up water and acquires a strongly acid flavour. (Engelhardt.) Neutral. (Pelouze.)

| *Crystals dried in vacuo.* | | | Engelhardt. |
|---|---|---|---|
| 12 C | 72 | 50·00 | 49·87 |
| 8 H | 8 | 5·56 | 5·67 |
| 8 O | 64 | 44·44 | 44·46 |
| $C^{12}H^{8}O^{8}$ | 144 | 100·00 | 100·00 |

The same result had previously been obtained by Gay-Lussac & Pelouze, and again by Pelouze.

*Decompositions.* 1. Lactide when suddenly heated suffers partial decomposition and assumes a yellow colour. (Corriol.) The products obtained at 250° are carbonic oxide, aldehyde, citraconic acid and lactide, the same therefore as from lactic anhydride. (Engelhardt). — 2. The vapours evolved from boiling lactide are inflammable and burn with a blue flame. (Gay-Lussac & Pelouze.)—3. Lactide is not altered by immersion in cold oil of vitriol, but when heated in that liquid, it blackens and disappears, with evolution of sulphurous acid. (Corriol.) — 4. It is converted, very slowly in damp air or in cold water, more quickly in hot water, but in any case less slowly than lactic anhydride [probably because it dissolves more easily], quickly also by aqueous alkalis (Pelouze), into ordinary lactic acid. (Gay-Lussac & Pelouze.)

*Combinations.* Lactide dissolves in boiling *water* more abundantly than lactic anhydride, and on cooling — provided it has not been converted by continued boiling into lactic acid — separates out for the most part (Gay-Lussac & Pelouze), in needles. (Engelhardt.)

It dissolves readily in *acetone.* (Pelouze.)

## Citric Acid.

$$C^{12}H^{8}O^{14} = C^{12}H^{8}O^{6},O^{8}.$$

SCHEELE de succo citri. *Opusc.,* 2, 181.
RETZIUS. *Crell. N. Entd.* 3, 193.
HERMBSTÄDT. *Phys. chem. Vers.* 1, 207.
DIZE. *J. de la Soc. des Pharmac.* T. 1, Nr. 6, 42; also *Scher. J.* 2, 707; also *A. Tr.* 6, 2, 205.
VAUQUELIN. *J. de la Soc. des Pharmac.* T, 1, Nr. 10, 83; also, *Scher. J.* 2, 712; also *A. Tr.* 7, 1, 89.
PROUST. *Scher. J.* 8, 613.
RICHTER. *N. Gegenst.* 1, 59 and 129; 6, 63.
BERZELIUS. *Gilb.* 40, 248. — *Ann. Chim.* 94, 171. — *Ann. Chim. Phys.* 67, 303; also *J. pr. chem.* 14, 350. — *Pogg.* 27, 281; — *Pogg.* 47, 309; also *Ann. Chim. Phys.* 70, 215; also *Ann. Pharm.* 30, 86; also *J. pr. chem.* 17, 177. — *Jahresber.* 21, 249.
LIEBIG. *Ann. Pharm.* 5, 134; 26, 119 and 152; 26, 118 and 151; 44, 57.
ROBIQUET. *Ann. Chim. Phys.* 65, 68; also *Ann. Pharm.* 25, 138; also *J. pr. chem.* 11, 66. — *J. Pharm.* 25, 77; also *Ann. Pharm.* 30, 229; also *J. pr. chem.* 17, 143.
WACKENRODER. *N. Br. Arch.* 23, 266.
MARCHAND. *J. pr. chem.* 23, 60.
W. HELDT. *Ann. Pharm.* 47, 57.
CAHOURS. *N. Ann. Chim. Phys.* 19, 488; also *J. pr. chem.* 41, 62; abstr. *Compt. rend.* 21, 814.
L. PEBAL. *Ann. Pharm.* 82, 78; abstr. *N. Ann. Chim. Phys.* 35, 469.— Further, *Ann. Pharm.* 98, 67.

*Citronsäure, Acide citrique.* Discovered by Scheele in 1784.

*Sources.* 1. In the free state, and mixed with little or no malic acid; in the fruit of *Citrus medica,* and *Citrus Aurantium,* of *Prunus Padus,*

*Vaccinium Vitis Idæa* and *Oxycoccos*, of *Rosa canina* and *Solanum Dulcamara* (Scheele); also in the unripe fruit of *Solanum Lycopensium* (Bertagnini, *Cimento*, 2, 308).— 2. Mixed with an equal quantity of malic acid: in the fruits of *Ribes Grossularia* and *rubrum*, of *Vaccinium Myrtillus*, *Cratægus Aria*, *Prunus Cerasus*, *Fragaria vesca*, *Rubus Idæus and Chamæmorus* (Scheele); also of *Sambucus racemosa*. (Thibierge.) — 3. With malic and tartaric acids; in the mark of tamarinds (Vauquelin), and in the berries of the mountain-ash. (Liebig). — 4. In the form of citrate of potash or lime : in the haulm of *Aconitum Lycoctonum*, *Convallaria majalis*, and *multiflora*, *Isatis tinctoria* and *Nicotiana Tabacum ;* in the milky juice of *Lactuca sativa* and *virosa ;* in the fruits of *Ribes Grossularia* and *Capsicum annuum*, in the root of *Asarum europæum*, and in the tubers of *Helianthus tuberosus* and *Dahlia pinnata*, in the bulbs of *Allium cepa*, in the alburnum of *Clematis Flammula*, and in the green walnut-shell. — Citric acid is also found, free or combined; in mangold-wurzel (Michaelis, *J. pr. chem.* 54, 184), in coffee-berries, in madder-root, and in *Calluna vulgaris* (Rochleder, *J. pr. chem.* 55, 385; 56, 93, 58, 189); in the haulm and root of *Richardsonia scabra*, (Rochleder & Willigk, *J. pr. chem.* 56, 72); in the haulm of *Asperula odorata* (Schwartz, *J. pr. chem.* 55, 398); in the leaves of *Physalis Alkekengi* (Dessaignes & Chautard, *N. J. Pharm.* 21, 24), *Rubia tinctorum* and *Ledum palustre* (Willigk, *Ann. Pharm.* 82, 339; 84, 363); also in fir-needles. (Kawalier, *Ann. Pharm.* 88, 360.)

*Preparation.* 1. Lemon juice is saturated with carbonate of lime, till it no longer reddens litmus; the liquid strained through linen; the citrate of lime which remains on the strainer washed with hot water, till the liquid runs through colourless; and digested with a quantity of oil of vitriol amounting to 60 per cent. of its weight in the dry state, diluted with eight times the quantity of water. The acid liquid filtered and evaporated yields the crystallised acid. (Scheele.)

In English manufactories, 10 pts. of citrate of lime are decomposed by a cold mixture of 9 pts. oil of vitriol and 56 pts. water; the liquid filtered; the gypsum washed with cold water; the filtrate boiled over an open fire till it attains the specific gravity of 1·13, then evaporated to a syrup in flat vessels placed over the water-bath; and this syrup, as soon as it becomes covered with a saline film, immediately cooled down to the crystallising point, before the excess of sulphuric acid converts it more or less into a black mass. The crystals are purified by three or four recrystallisations, and the mother-liquor, after dilution with water, treated with carbonate of lime, like fresh lemon-juice. (Berzelius, *Lehrb.*) — Martius (*Kastn. Arch.* 10, 486) in order to obtain a colourless acid, first clarifies the lemon-juice by boiling with white of egg, whereby it is nearly decolorised. Dizé purifies the acid from gypsum by solution in alcohol.— Gay-Lussac and Thénard purify it from adhering sulphuric acid by a method similar to that adopted for the purification of oxalic acid (ix, 113), viz. by digesting it with oxide or citrate of lead, then filtering, and precipitating the dissolved lead by sulphuretted hydrogen. — If the liquid, in consequence of too little sulphuric acid having been used, contains acid citrate of lime, no crystallisation takes place. (Scheele).— 2. Lemon-juice is neutralised with potash, and precipitated with neutral acetate of lead; the citrate of lead decomposed by long digestion with dilute sulphuric acid; the free sulphuric acid removed from the liquid by nitrate of baryta; and the filtrate evaporated to the crystallising point.

A similar process is adopted with currant-juice. (Richter). [But what becomes of the malic acid ?] — 3. Tilloy (*J Pharm.* 13, 305; also *N. Tr.* 16, 2, 193), presses bruised ripe currants, after the vinous fermentation is over; distils off the alcohol; saturates the acid of the residue with carbonate of lime; decomposes the washed sediment with an excess of warm dilute sulphuric acid; again saturates the filtrate, which contains a certain quantity of malic acid in addition to the citric, with carbonate of lime, after evaporating it a little; once more decomposes the washed citrate of lime with sulphuric acid; decolorises the filtrate with animal charcoal; filters, evaporates; filters from separated gypsum; and leaves the filtrate to crystallise at 25°. If the crystals are still coloured, the acid must be saturated a third time with carbonate of lime. 100 kilogrammes of currants yield 10 litres of alcohol of 20° Bm. and 1 kilogramme of citric acid; (*compare* Chevallier, *J. Chim. méd.*, 3, 265.)

By drying the hydrated crystals obtained by evaporation of the aqueous solution (or by cooling from a solution saturated while hot, according to Marchand), at 100° in the air (or at 16° in vacuo over chloride of calcium, according to Wackenroder, or over oil of vitriol, according to Marchand), the anhydrous acid is obtained. (Berzelius.)

*Properties.* White effloresced crystals; inodorous, very sour, reddening litmus strongly. (Berzelius.) Transparent crystals, still retaining the form of the hydrated acid. (Marchand.)

| *Crystals.* | | | Marchand, *a.* | Marchand, *b.* | Wackenroder, *a.* | Pebal. *c.* |
|---|---|---|---|---|---|---|
| 12 C | 72 | 37·50 | 37·87 | 37·71 | 37·97 | 37·61 |
| 8 H | 8 | 4·17 | 4·30 | 4·27 | 4·21 | 4·16 |
| 14 O | 112 | 58·33 | 57·83 | 58·02 | 57·82 | 58·23 |
| $C^{12}H^8O^{14}$ | 192 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 |

*a* obtained by drying the bihydrated, *b* by drying the monohydrated acid in a cold dry vacuum; *c* by drying the bihydrated acid at 100°.—Berzelius regards hypothetically anhydrous citric acid = Ci as $C^4H^2O^4$, and the dehydrated acid as $C^4H^2O^4 + \frac{2}{3}Aq$, which multiplied by 3, likewise gives $C^{12}H^8O^{14}$; according to Liebig, Ci = $C^{12}H^5O^{11}$.

*Decompositions.* 1. Monohydrated citric acid subjected at a gradually increasing temperature to *dry distillation*, fuses quietly at 150° (Robiquet); gives off at first carbonic acid and a small quantity of carbonic oxide, afterwards only the former (Robiquet); and yields a distillate consisting at first of tolerably pure water (Cahours), then of acetone, the production of which by this decomposition was first observed by Boullay & Robiquet. (Cahours.) At 150°, it yields a few needles (perhaps of aconitic acid) which sublime in the arch of the retort, and afterwards disappear (Robiquet); at 160, it exhibits an olive-green colour, and if cooled at this stage, dissolves completely in a small quantity of ether, but crystallises after a few hours in the form of ordinary citric acid no longer soluble in ether. The quantity of citric acid which thus crystallises is greater as the fusion has been continued for a shorter time (Robiquet), whereas, after a somewhat stronger fusion, the citric acid is for the most part converted into aconitic acid. (Dahlström.) At 175°, it yields first colourless, then pale yellow drops of oil, which are given off more abundantly at 195°, together with a small quantity of watery

liquid, but at 210°, are free from watery liquid and almost colourless; at 240° they pass over yellow. (Robiquet.) The coloured thickish residue, heated to 170°, gives off a small quantity of colourless oil, and after it has assumed a transparent, hyacinth-red, aloe-like aspect, and appears somewhat viscid after cooling, gives off at a higher temperature, a brown empyreumatic oil, in smoky vapours, and finally a soft yellow fatty substance, while charcoal remains behind. — The water and empyreumatic-tasting oily distillates thus obtained increase continually in specific gravity (from 1·0555 to 1·300), and in amount of acid. The first contains acetone; the following portions, a continually increasing quantity of citraconic acid at first dissolved in water; while the last contains the same acid deprived of its water so far as to convert it into citraconic anhydride, mixed, towards the end of the distillation, with a continually increasing quantity of empyreumatic oil (black and pitchy according to Liebig) having a disagreeable taste and odour. (Robiquet.)

Citric acid when heated for a comparatively short time, is converted into a brown deliquescent mass; but if the heat be continued, it becomes continually browner, gives off carbonic acid and carbonic oxide, and yields as distillates, first water, then, in white and ultimately in brown fumes, a colourless aqueous solution of citraconic acid (free from citric and acetic acid) and an oil which has a bituminous odour, a sharp sour taste, and settles down to the bottom of the watery liquid [citraconic anhydride with a small quantity of pitch], while a light and highly lustrous charcoal remains behind. (Lassaigne, *Ann. Chim. Phys.* 21, 102). — The hydrated acid heated as quickly as the frothing allows, gives off water, then, in white fumes, acetone and carbonic oxide (the residue consisting of undecomposed citric acid, and matter which does not crystallise from water); then, while the fumes diminish and the carbonic oxide is continually more replaced by carbonic acid, a colourless, acid liquid, rich in acetone; and when drops of oil begin to pass over, the residue consists of aconitic acid mixed with a small quantity of citric acid, and exhibiting, when the distillation is continued, the decomposition described at page 404. (Crasso.) — By rapid distillation, no carbonic oxide or acetic acid is obtained, both of these products however being formed by slow distillation. — According to Baup (*Ann. Chim. Phys.* 61, 182), the acid distillate consists of citraconic acid (x, 417); with a small quantity of itaconic acid (x, 424); according to Crasso, the proportion is the reverse of this; Liebig was unable to find any difference between the two acids. The dry distillation of pure citric acid begins only at 175° [?]; but the acid mixed with pumice-stone begins to distil at 155°, yielding carbonic acid gas free from carbonic oxide; and when mixed with spongy platinum, it begins to distil at 166°, and yields carbonic acid mixed with only a very small quantity of carbonic oxide: Contact-action. (Reiset & Millon, *N. Ann. Chim. Phys.* 9, 289). — The very small quantity of charcoal which citric acid leaves, appears even when the acid is distilled with the greatest care in vacuo. (Dumas, *Ann. Chim. Phys.* 52, 295.) The decompositions are perhaps:

$$C^{12}H^8O^{14} - 2HO = C^{12}H^6O^{12} \text{ (aconitic acid).}$$

$$C^{12}H^8O^{14} - 2CO^2 - 2HO = C^{10}H^6O^8 \text{ (citraconic and itaconic acids).}$$

$$C^{12}H^8O^{14} - 4CO^2 - 2CO - 2HO = C^6H^6O^2 \text{ (acetone).}$$

2. Chlorine gas passed through the concentrated acid, which absorbs it slowly in the shade, more quickly in sunshine, very slowly precipitates

an oil, without evolution of carbonic acid. This oil, when rectified, is colourless; has a density of 1·75; boils at 200°; has a peculiar irritating odour, but does not attack the eyes; has a sweetish burning taste; reddens moist litmus paper after some time, and forms with water, a hydrate which crystallises in laminæ at 6°. The oil is $C^8Cl^8O^3$, and its hydrate is $C^8Cl^8O^3.3Aq$. [?] (Plantamour, *Berz. Jahresber.* 26, 428.) Städeler (*Chem. Gaz.* 1853, 341) regards the oil as hexachlorinated acetone $C^6Cl^6O^2$, and the hydrate as $C^6Cl^6O^2,2Aq$. According to Laurent the oil is $C^{10}Cl^{10}O^4$: for,

$$C^{12}H^8O^{14} + 12Cl = C^{10}Cl^{10}O^4 + 6HO + 2HCl + 2CO^2.$$

Chlorine gas acts but slowly on a concentrated solution of citrate of soda, even in sunshine, giving off carbonic acid, and a sweet ethereal odour, which at last becomes intolerably sharp, and precipitating from the turbid liquid, radiating crystals of monocitrate of soda and an oil. — 1. This oil, distilled fractionally after washing with water, gives off chloroform at 60°, then at 189°, a peculiar oil, and at 200°, an oil which appears to be a mixture of the peculiar oil with that which is produced (as above described) from the free acid. — The *peculiar* oil, which may easily be freed from fumes of hydrochloric acid by leaving it over lime in vacuo, is colourless, thin, of sp. gr. 1·66, boils steadily at 190°, has an extremely, pungent odour, excites tears, has a burning taste, is insoluble in water, and = $C^5Cl^4O^2$ [or $C^{10}Cl^8O^4$]. Both the peculiar oil, and that which is obtained from the free acid, decompose with rise of temperature in contact with alcoholic potash, forming chloride of potassium, and afterwards bichloroxalate of potash, $KO,C^4Cl^2O^3$, which crystallises in shining scales and dissolves readily in water (compare however x, 142). — 2. The watery liquid separated from the oily mixture yields by distillation, chiefly elayl-oxalic acid, isomeric with succinic acid, whose silver salt is $AgO,C^4H^2O^3$ [ = $C^8H^4Ag^2O^8$]. (Plantamour, *Berz. Jahresber.* 26, 428). Observations by Laurent (*Compt. rend.* 26, 36.)

¶. Dried citric acid in contact with pentachloride of phosphorus, becomes heated, and yields oxychlorocitric acid and oxychloride of phosphorus;

$$C^{12}H^8O^{14} + PCl^5 = C^{12}H^8O^{12}Cl^2 + PCl^3O^2.$$

If the mixture be heated, hydrochloric acid is evolved, and chloride of citryl appears to be formed;

$$C^{12}H^8O^{12}Cl^2 + 2PCl^5 = C^{12}H^5O^8Cl^3 + 2PCl^3O^2 + 3HCl.$$

Lastly, if the heat be continued, the liquid assumes a deep cherry-red colour and then appears to contain chloride of aconityl:

$$C^{12}H^5O^8Cl^3 + PCl^5 = C^{12}H^3O^6Cl^3 + PCl^3O^2 + 2HCl.$$

(Pebal, *Ann. Pharm.* 98, 76.) ¶.

3. *Bromine* gradually added to a concentrated aqueous solution of citrate of potash (soda, or baryta), till the effervescence arising from escape of pure carbonic acid ceases, dissolves rapidly, with rise of temperature, and forms a red liquid, from which, after the excess of bromine has been removed by water, dilute potash cautiously added, throws down a colourless oily mixture of bromoform (vii, 339), bromoxaform (ix, 190), and a small quantity of a third substance, while bromide of potassium

remains in solution. — Citrate of ammonia treated with bromine also produces a large quantity of carbonic acid, but not a trace of oil. (Cahours.)

4. Aqueous *iodic acid* boiled for several hours with citric acid, converts part of the carbon by oxidation into carbonic acid. (Millon, *Compt. rend.* 19, 271.)

5. Citric acid treated with 3 pts. of *nitric acid* yields $\frac{1}{3}$ pt. of oxalic acid, but only at the boiling heat and very slowly; with 5 pts. of nitric acid, $\frac{1}{4}$; and with 10 pts., no oxalic but only acetic acid. (Westrumb.)

6. Pulverised dry citric acid dissolves in 12 pts. of cold *oil of vitriol,* forming a colourless liquid, which, between 25° and 30°, gives off carbonic oxide in very small bubbles, and mixed with a very small quantity of carburetted hydrogen; then from 40° upwards, carbonic oxide with a continually increasing proportion of carbonic acid, which from 75° upwards, completely replaces the carbonic oxide, but is not mixed with sulphurous acid till the temperature rises to 100°. At 100°, the liquid, which was before pale yellow, acquires a reddish colour; has suffered a loss of weight amounting to between 53 and 55 per cent. of the dry acid; gives off when mixed with water an odour of acetone (likewise observed by Gerhardt, *Compt. rend.* 17, 314); yields, when saturated with carbonate of soda, a very scanty, brown, friable, resinous precipitate (which dissolves, with rose-red colour, in alkalis and alcohol, and is the cause of the red colouring of the sulphuric acid liquid); and when filtered therefrom and evaporated, yields reddish crystals of Glauber's salt, and a brown mother-liquor containing, in combination with soda, a brown viscid acid, which does not precipitate baryta and lime, and forms with them uncrystallisable salts. (Robiquet.) Citric acid exposed to a continually increasing heat in contact with excess of oil of vitriol, gives off a very large quantity of carbonic oxide. (Dumas.)

7. Aqueous citrate of potash reduces *gold* from its hydrochloric acid solution, without formation of carbonic acid. (Pelletier.) — The aqueous acid treated with *peroxide of manganese* gives off carbonic acid. (Scheele.) — It reduces *vanadic acid* to vanadic oxide. (Berzelius.) It converts *mercuric oxide,* with brisk effervescence, into a solid mass which appears to contain acetic acid. (Vauquelin.) — Citric acid which has been kept for some time in a state of fusion, and then pulverised after cooling, becomes strongly incandescent, when quickly triturated with *peroxide of lead* at 23°; this effect is not produced by the bihydrated acid, even after it has effloresced. (R. Böttger, *J. pr. Chem.* 8, 477.)

8. Citric acid fused with *hydrate of potash* forms oxalic acid. (Gay-Lussac.) It is then resolved into 1 At. oxalic acid and 2 At. acetic acid:

$$C^{12}H^8O^{14} + 2HO = C^4H^2O^8 + 2C^4H^4O^4.$$

(Liebig, *Ann. Pharm.* 26, 158.)

9. The dry acid heated with potassium or sodium, yields alkali and charcoal, without incandescence. (Gay-Lussac & Thénard.)

10. A dilute aqueous solution of citric acid decomposes, even in close vessels, with formation of fungi. (Berzelius.) — Wittstein (*N. Jahrb. Pharm.* 2, 229) found the solution to keep for three years without alteration. —A supposed conversion of lemon-juice kept in bottles into tartaric acid is mentioned by Schlindler. (*Repert.* 31, 280.) — ¶. Clarified lemon-juice saturated with carbonate of lime, ferments, after standing for a day or two at a temperature between 30° and 35°, giving off carbonic acid and hydrogen

in variable proportions and forming acetic and butyric acids. The same effect takes place more quickly with unclarified lemon-juice neutralised with carbonate of lime, and still more quickly with pure citrate of lime, mixed with a small quantity of beer-yeast. (Personne, *Compt. rend.* 36, 197.) — Crystallised citric acid made into a thin paste with carbonate of lime and water, mixed with a quantity of putrefying curd equal to $\frac{1}{4}$ the weight of the acid, and left in a bottle provided with a gas-delivery tube at a temperature varying from 27° to 38°, attained in three days a state of stinking putrefaction, which appeared to reach its maximum in ten days. The gas then evolved contained about 2 vol. carbonic acid to 1 vol. hydrogen; at a later stage, the evolution of gas became weaker and the proportion of hydrogen greater; amounting at last to $\frac{3}{4}$ of the volume of the gas. The products formed after 22 days contained no succinic acid, but propionic and acetic acids, which, when neutralised with bases, yielded aceto-propionates (ix,408.) In a second experiment, when citric acid was mixed up to the consistence of a thin paste, with carbonate of lime-water and $\frac{1}{6}$ of its weight of putrefying curd, and the mixture left for three or four weeks at 38° in an open vessel, the only product formed was acetic acid. (H. How, *Chem. Soc. Qu. J.* 5, 1.) ¶.

*Combinations. a. Mono-hydrated Citric acid* $C^{12}H^{9}O^{15}$ [?]. — Water saturated at 100° with citric acid yields by slow cooling to 4°, translucent crystals. (Berzelius.) — Wackenroder obtained by this process, sometimes no crystals, sometimes crystals having the form of the following hydrate; but Marchand, by boiling the solution till a crystalline crust began to form, and then cooling it, certainly obtained the crystals $C^{12}H^{9}O^{15}$, which likewise belonged to the right prismatic system, like the crystals of $C^{12}H^{10}O^{16}$, but yet, according to G. Rose, exhibited a different form. — The powder of the crystals, after drying in the air at 16°, does not give off any thing at 100°, and melts quietly at a stronger heat, forming a transparent colourless liquid, which solidifies into a glass on cooling. When dried with oxide of lead, it gives off 14 per cent. of water. (Berzelius.) [As the lead-salt retains 1 At. water, the calculation is 201 : 27 = 100 : 13·43]. The crystals left in a cold vacuum, give off, *without turbidity*, from 2·2 to 2·3 per cent. of water, so that $C^{12}H^{8}O^{14}$ remains; and an equal quantity when exposed to dry air, or evaporated with oxide of lead and water, or when dried for a short time at 100°. (Marchand.)

| | *Crystals.* | | Marchand. |
|---|---|---|---|
| 12 C | 72 | 35·82 | 36·54 |
| 9 H | 9 | 4·48 | 4·33 |
| 15 O | 120 | 59·70 | 59·13 |
| $C^{12}H^{9}O^{15}$ | 201 | 100·00 | 100·00 |

| | | |
|---|---|---|
| $C^{12}H^{8}O^{12}$ | 192 | 95·52 |
| HO | 9 | 4·48 |
| $C^{12}H^{8}O^{12}$,Aq | 201 | 100·00 |

*b. Bihydrated Citric acid,* $C^{12}H^{10}O^{16}$ [?]. — The commercial acid. — Crystallizes by spontaneous evaporation of the aqueous solution (between

16° and 30° according to Wackenroder) in large transparent colourless prisms. (Berzelius.) Prisms belonging to the right prismatic system. (Fig. 79.) Cleavage parallel to $u$ and $t$; $u' : u = 101°\ 30'$; $u' : t = 129°\ 15'$; $u' : u = 163°\ 23'$; $n : n = 134°\ 45'$; $y : y$ below $= 111°\ 50'$; $t : a = 139°\ 45'$; $t : i = 121°\ 15'$; $i : i = 117°\ 30'$. —(Brooke, *Ann. Phil.* 22, 119; *compare* Wackenroder, *J. pr. Chem.* 23, 206; also Heusser, *Pogg.* 88, 127.) — Sp. gr. 1·617. (Richter.) — The crystals effloresce in the air between 28° and 50°. (Berzelius.) When perfectly dried in vacuo over chloride of calcium at 40°, they remain *quite clear*. (Wackenroder.) Their powder dried for 24 hours, first at 40° and at last gradually at 100°, in contact with the air, gives off 8·5 per cent. of water, and appears tumefied. When directly heated to 100°, it suffers the same loss, and appears fused and translucent in the middle; when evaporated with oxide of lead, it gives off 17 p. c. (17·03 p. c. according to Marchand,) [4 At.] water. (Berzelius.) When dried in vacuo over oil of vitriol at ordinary temperatures, it gives off 8·38 per cent. of water. (Marchand.)

| | | | Prout. | Marchand. a. | b. |
|---|---|---|---|---|---|
| *Crystals.* | | | | | |
| 12 C | 72 | 34·29 | 34·28 | 33·91 | 34·02 |
| 10 H | 10 | 4·76 | 4·76 | 4·84 | 4·67 |
| 16 O | 128 | 60·95 | 60·96 | 61·25 | 61·31 |
| $C^{12}H^{10}O^{16}$ | 210 | 100·00 | 100·00 | 100·00 | 100·00 |

| | | | Marchand. |
|---|---|---|---|
| $C^{12}H^{8}O^{14}$ | 192 | 91·43 | 91·62 |
| 2 HO | 18 | 8·57 | 8·38 |
| $C^{12}H^{8}O^{14} + 2Aq$ | 210 | 100·00 | 100·00 |

*a.* Commercial acid, after its powder has been strongly pressed between bibulous paper; *b.* The same from solution in water by evaporation below 50°, recrystallised and pressed.

The acid pulverised and dried in the air at 30°, gives off 7·2 p.c. water, when gradually heated in the air to about 109°; it is then baked together but not melted; fuses completely at 153°, with formation of bubbles and loss of 2·4 per cent. not of water but of volatile acids (and acetone), and after cooling yields an amber-coloured, hard, inflated glass. — The crystals when completely dried in the air at a moderate heat, appear dull on the surface, and give off a trace of water when melted, that is to say above 120°; they reabsorb their water in cold air. — The undried crystals melt very easily, often below 100°, forming a transparent colourless liquid, which remains soft after cooling, and crystallises at 16° after some hours in a partly laminar, partly fibrous mass (whereas the dried acid, when cooled after fusion, is tolerably hard and brittle, but somewhat inflated and yellowish); it begins to boil at 150°, the ebullition increasing up to 170°, at which temperature the acid completely loses its water and becomes lemon-yellow; then between 180° and 190°, it gives off gas with violence, assumes a brownish-yellow colour, and on cooling yields a clear viscid mass, on which, when exposed to the air for a few days, needles (probably of aconitic acid) are produced. From all this it may be concluded that crystallised citric acid never contains combined water,

but is anhydrous, and contains water [or mother-liquor] mechanically enclosed within it, which water it absorbs again when exposed to the air after drying. (Wackenroder.) — This view does not perhaps appear quite consistent with the constant composition of the bihydrated acid; but on the other hand it is strongly corroborated by the fact that both kinds of crystals, when left in a cold dry space either exhausted or filled with air, give off the whole of their water without becoming turbid. The crystals, according as they are more or less quickly formed, may have more or less liquid mechanically enclosed within them, so that they sometimes appear to contain 1 At. sometimes 2 At. of chemically combined water. That Berzelius did not obtain any more water at 100° from the monohydrated crystals, after their powder had been dried in the air at 16° (whereas, accord to Marchand, the crystals give off 2·2 p. c. in a cold vacuum) may perhaps be explained by supposing that they had already lost the whole of their water by exposure to the air at 16°. Berzelius was led by this experiment to suppose that the crystals $C^{12}H^{9}O^{15}$ do not give off any water at 100°, and that Gmelin must have had these crystals before him when he remarked (*Handb. Ausg.* 3, ii, 86), that "the crystallised acid exposed for several days to the heat of the water-bath, does not suffer any loss of weight or become turbid, and should perhaps, like crystallised tartaric acid, be regarded as anhydrous;"—whereas the acid which the author examined with respect to its amount of water, was *commercial* acid which had been kept for several years in a loosely-stoppered bottle, and had there perhaps become thoroughly dry. The crystallised acid is probably therefore anhydrous, but contains mechanically enclosed mother-liquor, which it loses even by exposure to cold dry air, but forms with it when heated to fusion,—which takes place the more easily as the crystals contain more mother-liquor,—a compound which retains its water with greater force.

c. *Aqueous Citric acid.* — The acid deliquesces completely in very damp air. (Wackenroder.) It dissolves in $\frac{3}{4}$ pt. of cold, in $\frac{1}{2}$ pt. of hot water (Vauquelin), producing fall of temperature (Dizé) and forming a syrup.

100 pts. of solution contain of crystalline acid, according to Richter :

| *Sp. gr.* | *Acid.* | *Sp. gr.* | *Acid.* | *Sp. gr.* | *Acid.* | *Sp. gr.* | *Acid.* |
|---|---|---|---|---|---|---|---|
| 1·30 .... | 60·32 .... | 1·22 .... | 45·33 .... | 1·14 .... | 30·46 .... | 1·06 .... | 14·06 |
| 1·28 .... | 56·80 .... | 1·20 .... | 41·72 .... | 1·12 .... | 26·72 .... | 1·04 .... | 9·56 |
| 1·26 .... | 53·17 .... | 1·18 .... | 38·16 .... | 1·10 .... | 22·63 .... | 1·02 .... | 4·87 |
| 1·24 .... | 49·42 .... | 1·16 .... | 34·49 .... | 1·08 .... | 18·40 | | |

The *Citrates* are divided, since citric acid is a tribasic acid, into *tribasic* (neutral) $C^{12}H^{5}M^{3}O^{14}$, *bibasic*, $C^{12}H^{6}M^{2}O^{14}$, and monobasic $C^{12}H^{7}MO^{14}$. Berzelius regards the hypothetical anhydrous acid as $C^{4}H^{2}O^{4}$, so that, according to him, the tribasic salts are MO, $C^{4}H^{2}O^{4}$ (or multiplied by 3, $= 3(MO, C^{4}H^{2}O^{4}) = C^{12}H^{6}M^{3}O^{15}$), but as he found in 1832, that these three-atom salts, when dried at a high temperature (from 100° to 190°, according to the salt), lose another atom of water, and are reduced to $C^{12}H^{5}M^{3}O^{14}$, he subsequently supposed that in drying, $\frac{1}{3}$ of the citric acid is converted into 1 At. of hypothetical anhydrous aconitic acid, which he regarded as $C^{4}HO^{3}$, so that the highly dried salt would be a mixture of 1 At. aconitate and 2 At. citrate; and lastly, as the salt thus dried redissolves in water as an ordinary citrate, he was obliged to assume, that aconitic acid, in presence of citrates, takes up another atom of water, and is reconverted into citric acid, whereas there is no known instance of the conversion of actual aconitates into citrates by the action of water. These difficulties were com-

pletely removed by Liebig's demonstration, in 1837, of the tribasic nature of citric acid, fixing the atom at $C^{12}H^8O^{14}$. — The citrates decompose at 230° and upwards. (Berzelius.) When subjected to dry distillation, they froth up, give off empyreumatic acid, and leave a large quantity of charcoal. (Vauquelin.) — When heated with oil of vitriol, they give off carbonic oxide and acetic acid. (Liebig, Pogg, 28, 199.) — Their aqueous solution decomposes by keeping, with formation of mucous flakes. The saturated aqueous solution of citrate of ammonia or potash, mixed with citric or any other acid, yields a non-crystalline precipitate; the solution of citrate of ammonia, potash, or soda, mixed with lime-salts and heated, yields a copious precipitate soluble in a large quantity of water, as well as in acetic acid. (Vauquelin.) Many citrates obtained by precipitation dissolve in aqueous solutions of the alkaline citrates, and the lead-precipitate, after washing, dissolves in ammonia. (Berzelius.)

*Citrate of ammonia.* — *a. Tribasic.* — The boiling alcoholic solution of the acid, neutralised with ammonia, becomes turbid on cooling, and deposits the salt in oily drops which do not crystallise. (Heldt.)

*b. Bibasic.* — The acid neutralised with ammonia yields by hot evaporation, as well as by spontaneous evaporation, with loss of part of the ammonia, rhombic prisms, which taste pleasantly acid, and afterwards bitter and cooling; do not lose weight at 100; become moist by contact with the air; and separate on cooling from a boiling alcoholic solution in oily drops. (Heldt.) Deliquescent prisms, which give off ammonia at a high temperature. (Scheele.) The same crystals are obtained by evaporating the solution of the neutral citrate mixed with half as much citric acid as it already contains. (J. C. Heusser, *Pogg.* 88, 121. See also this paper for the crystalline form.)

| *Crystals.* | | | Heldt. |
|---|---|---|---|
| 12 C | 72 | 31·86 | 32·26 |
| 2 N | 28 | 12·39 | 12·40 |
| 14 H | 14 | 6·19 | 6·24 |
| 14 O | 112 | 49·56 | 49·10 |
| $C^{12}H^6(NH^4)^2O^{14}$ | 226 | 100·00 | 100·00 |

*Monobasic.* $C^{12}H^7(NH^4)O^{14}$. — A solution of citric acid neutralised with ammonia, and then mixed with twice as much citric acid as it already contains, yields this salt by spontaneous evaporation, in doubly oblique prismatic crystals. (Heusser.) Heldt did not succeed in preparing the monobasic salt.—Heusser, by mixing a solution of citric acid neutralised with carbonate of ammonia, with a quantity of citric acid equal to that which it already contained, obtained by spontaneous evaporation, doubly oblique prismatic crystals, to which he assigns the formula $NH^4O,C^4H^2O^4$.

*Citrate of potash.* — *a. Tribasic.* — The aqueous acid neutralised with carbonate of potash yields by spontaneous evaporation, transparent, colourless needles, united in stellate groups; they have an alkaline taste, give off 5·7 p.c. (2 At.) water at 200°, and 8·2 p.c. at 230°, decomposing however partially and assuming a yellowish brown colour. The salt deliquesces readily on exposure to the air; it is insoluble in absolute alcohol, but forms with hydrated alcohol, an aqueous solution above which is a layer of dehydrated alcohol. (Heldt.)

| | *Crystals.* | | Heldt. |
|---|---|---|---|
| 12 C | 72·0 | 22·18 | 22·29 |
| 7 H | 7·0 | 2·16 | 2 34 |
| 3 KO | 141·6 | 43·62 | 43·35 |
| 13 O | 104·0 | 32·04 | 32·02 |
| $C^{12}H^{5}K^{3}O^{14}$, + 2Aq | 324·6 | 100·00 | 100·00 |

*b. Bibasic.* — A solution of 2 pts. of the acid, exactly neutralised with carbonate of potash, yields, when mixed with 1 pt. more of the acid, and then left to evaporate, an amorphous crust having a sour taste, and behaving with alcohol like the salt *a* (Heldt). Crystals belonging to the oblique prismatic system. (Heusser.)

| | | | Heldt. |
|---|---|---|---|
| 12 C | 72·0 | 26·83 | 27·14 |
| 6 H | 6·0 | 2·24 | 2·28 |
| 2 KO | 94·4 | 35·17 | 34·98 |
| 12 O | 96·0 | 35·76 | 35·60 |
| $C^{12}H^{6}K^{2}O^{14}$ | 268·4 | 100·00 | 100·00 |

*c. Monobasic.* — 1 pt. of the acid is exactly neutralised with carbonate of potash, 1 pt. [2 pts.?] of the acid added, and the solution left to evaporate at 40°. Large, transparent prisms, permanent in the air, and having an agreeably sour taste. They melt in their water of crystallisation at 100°, ultimately giving off 13·81 p.c. (4 At.) water and forming a gummy liquid, which, on cooling, solidifies completely into a concentric radiated mass of needle-shaped crystals, consisting of $C^{12}H^{7}KO^{14}$, and decomposes at 150°. The salt dissolves slightly in boiling alcohol, and crystallises therefrom on cooling. (Heldt.)

| | *Crystals.* | | Heldt. |
|---|---|---|---|
| 12 C | 72·0 | 27·05 | 27·18 |
| 11 H | 11·0 | 4·13 | 4·19 |
| KO | 47·2 | 17·73 | 17·43 |
| 17 O | 136 0 | 51·09 | 51·20 |
| $C^{12}H^{7}KO^{14}$, + 4Aq | 266·2 | 100·00 | 100·00 |

*Citrate of potash and ammonia.* — An aqueous solution of bibasic citrate of potash, mixed with excess of ammonia and evaporated, yields transparent, quickly deliquescing prisms united in radiated groups. (Heldt.)

| | *Crystals.* | | Heldt. |
|---|---|---|---|
| 12 C | 72·0 | 25·23 | 26·60 |
| N | 14·0 | 4·90 | |
| 9 H | 9·0 | 3·15 | 3·65 |
| 2 KO | 94·4 | 33·08 | 26·51 |
| 12 O | 96·0 | 33·64 | |
| $C^{12}H^{5}(NH^{4})K^{2}O^{14}$ | 285·4 | 100·00 | |

Heldt prefers the formula $3KO,\overline{Ci} + 2NH^{4}O,HO,\overline{Ci}$.

*Citrate of soda.* — *a. Tribasic.* — Crystallises from the syrupy solution by spontaneous evaporation in large opaque, rhombic prisms, which quickly effloresce, and are sparingly soluble in alcohol. (Heldt.) [For the crystalline form *vid.* Heusser, *Pogg.* 88, 121; also Schabus, *Jahresber*, 1854, 402.] The crystals have an agreeable saline taste, are permanent in the air, give off 17·5 p.c. [7 At.] water at 100° in a current of air, merely becoming translucent [and are reduced to $C^{12}H^9Na^3O^{18}$]; but from 190° to 200°, they give off 12·32 [4 At.] more (or 10·15 p. c. more of the weight of the fresh crystals; Heldt also estimates the loss which the crystals undergo at 200°, at 27·8 per cent.) and become opaque and milk-white [reduced to $C^{12}H^5Na^3O^{14}$], but dissolve in water in the form of the preceding salt. When the dry salt is dissolved in alcohol, only a trace of a salt remains behind, which appears to be aconitate of soda. (Berzelius.) — The crystals dissolve in $1\frac{3}{4}$ pts. of cold water (Vauquelin) and sparingly in alcohol. (Heldt.)

| *Dried at* 200°. | | |
|---|---|---|
| 12 C | 72·0 | 27·84 |
| 5 H | 5·0 | 1·93 |
| 3 NaO | 93·6 | 36·20 |
| 11 O | 88·0 | 34·03 |
| $C^{12}H^5Na^3O^{14}$ | 258·6 | 100·00 |

| *Crystals.* | | | Heldt. |
|---|---|---|---|
| 12 C | 72·0 | 20·13 | 20·34 |
| 16 H | 16·0 | 4·47 | 5·35 |
| 3 NaO | 93·6 | 26·18 | |
| 22 O | 176·0 | 49·22 | |
| $C^{12}H^5Na^3O^{14}$ + 11Aq | 357·6 | 100·00 | |

*b. Bibasic.* — When 2 pts. of the acid neutralised with soda are mixed with 1 pt. more of the acid, and the solution left to evaporate, it is almost wholly converted into needles having an agreeably sour taste and permanent in the air. (Berzelius.) The needles are transparent, and grouped in stars. (Heldt.)

| *Crystals.* | | | Heldt. |
|---|---|---|---|
| 12 C | 72·0 | 28·30 | 28·96 |
| 8 H | 8·0 | 3·14 | 3·29 |
| 2 NaO | 62·4 | 24·53 | 24 14 |
| 14 O | 112·0 | 44·03 | 43·61 |
| $C^{12}H^6Na^2O^{14}$, + 2Aq | 254·4 | 100·00 | 100·00 |

*c. Monobasic.* — The solution left to evaporate in a warm place becomes gummy and then crystallises completely in transparent needles grouped in stars. (Heldt.) — Berzelius, by evaporating 1 pt. of the acid neutralised with soda with 1 pt. more of the acid (in which case, according to Berzelius's view, 2 At. of the acid were mixed with 1 At. soda, but according to the view here adopted, 2 At. acid with 3 At. soda), obtained a transparent gum which ultimately became crystalline.

| *Needles.* | | | Heldt. |
|---|---|---|---|
| 12 C | 72·0 | 31·01 | 31·16 |
| 9 H | 9·0 | 3·87 | 3·96 |
| NaO | 31·2 | 13·44 | 13·12 |
| 15 O | 120·0 | 51·68 | 51·40 |
| $C^{12}H^{7}NaO^{14}, + 2Aq$ | 232·2 | 100·00 | 100·00 |

*Citrate of Soda and Ammonia.* — Crystalline crust. (Heldt.)

*Citrate of Soda and Potash.*— Aqueous bibasic citrate of soda neutralised with potash, yields, by spontaneous evaporation, separate crystals of tribasic citrate of soda, and tribasic citrate of potash. But a solution of the two salts in equal numbers of atoms yields, after a few days, stellate groups of silky needles of the double salt, which contain 21·77 p.c. C and 3·43 H, and after drying at 200°, at which temperature they give off 17·28 per cent. of water, they contain 26·00 C and 1·90 H; their residue dried at 200° leaves, when ignited, 64·31 p. c. carbonate of potash and soda. Therefore perhaps $C^{12}H^{5}K^{3}O^{14},C^{12}H^{5}Na^{3}O^{14} + 13Aq$. (Heldt.)

*Citrate of Lithia.* — *a. Tribasic.* — Amorphous, limpid, hard mass. — *b. Acid.* — Not crystallisable. (Berzelius.)

*Citrate of Baryta.* — *a. Tribasic.* — 1. The acid added to an excess of baryta-water throws down flakes, which become somewhat crystalline when heated. (Heldt.) — If the mixture contained rather too much acid, the excess goes into the precipitate, which however may be rendered neutral by digestion with baryta-water. (Berzelius.) — The salt dried in the air at 16°, gives off at 100° about half its water, at 150° in a current of air, nearly the whole, viz. 11·96 p. c. [6 At.], and at 190° in a current of air, the whole, viz. 13·9 p. c. [7 At.]. When covered with water and dried at a temperature somewhat above 100°, it recovers the weight of 88·04 p. c. (Berzelius.) — The salt precipitated either cold or hot, according to (2), and dried cold over oil of vitriol, gives off at 200°, 13·7 p. c. of water. (Heldt.) White powder, which dissolves very sparingly in water, readily in citric acid. (Scheele, Vauquelin.) The salt precipitated in the cold dissolves in water; but the salt precipitated from a hot solution, though it differs from the former only by containing a smaller quantity of water, is nearly or quite insoluble. (Liebig.)

| *Dried at* 200°. | | |
|---|---|---|
| 12 C | 72·0 | 18·24 |
| 5 H | 5·0 | 1·26 |
| 3 BaO | 229·8 | 58·21 |
| 11 O | 88·0 | 22·29 |
| $C^{12}H^{5}BaO^{14}$ | 394·8 | 100·00 |

| *Dried cold over oil of vitriol.* | | | Heldt. |
|---|---|---|---|
| 12 C | 72·0 | 15·73 | 15·76 |
| 12 H | 12·0 | 2·62 | 2·81 |
| 3 BaO | 229·8 | 50·20 | |
| 18 O | 144·0 | 31·45 | |
| $C^{12}H^{5}BaO^{14} + 7Aq$ | 457·8 | 100·00 | |

*b. With* 5 *At. base to* 2 *At. acid.* — 1. A hot aqueous solution of citric acid is completely saturated with the salt *a*, diluted with cold water, filtered from undissolved salt *a*, and evaporated. (Berzelius, Heldt.) — 2. Acetate of baryta is added to a boiling solution of citric acid, as long as the precipitate redissolves, and the filtrate evaporated, whereupon the salt which crystallises on the surface falls to the bottom. (Berzelius.) — The salt *a* is added to a boiling transparent mixture of citric acid and chloride of barium, as long as the resulting precipitate redissolves, and the solution left to crystallise by cooling. (Berzelius, Heldt.) — The white crystalline powder thus formed, gives off at 100° only a little hygroscopic water, and then contains 49·28 p. c. baryta. (Berzelius.) It gives off but little water at 100°, but 7·75 p. c. at 160°, and decomposes at 190°. (Heldt.)

*Dried at* 160.

| | | |
|---|---|---|
| 24 C | 144 | 19·94 |
| 11 H | 11 | 1·52 |
| 5 BaO | 383 | 53·05 |
| 23 O | 184 | 25·49 |
| $C^{12}H^5Ba^3O^{14},C^{12}H^6Ba^2O^{14}$ | 722 | 100·00 |

| *Air-dried.* | | | Heldt. |
|---|---|---|---|
| 24 C | 144 | 18·35 | 18·55 |
| 18 H | 18 | 2·29 | 2·34 |
| 5 BaO | 383 | 48·79 | |
| 30 O | 240 | 30·57 | |
| $C^{12}H^5Ba^3O^{14},C^{12}H^6Ba^2O^{14} + 7Aq$ | 785 | 100·00 | |

*c. Monobasic?* — The mother-liquor which remains in the preparation (1) of salt *b* leaves, when evaporated, a transparent gum (with a few crystalline points, according to Heldt), which tastes like cream of tartar, and dissolves readily in water; its solution in ammonia deposits on evaporation, iridescent scales of a salt containing ammonia and baryta. (Berzelius.)

As citrate of soda forms a precipitate only with a large quantity of chloride of barium, unless the liquid is heated, it follows that citrate of baryta must be soluble in a cold solution of citrate of soda. — Bibasic or monobasic citrate of potash or soda neutralised with baryta-water remains clear at first, but becomes turbid in a few minutes and deposits citrate of baryta. (Heldt.)

*Citrate of Strontia.* — *a. Tribasic.* — Strontia-water is precipitated by citric acid, or by a soluble alkaline citrate, in thick white flakes, which do not become crystalline when heated; give off, after drying in the air, 12·2 p. c. (5 At.) water at 210°, dissolve readily in hydrochloric and sparingly in acetic acid, and are precipitated therefrom by ammonia on boiling. (Heldt.)

*Dried at* 210.

| | | |
|---|---|---|
| 12 C | 72 | 22·43 |
| 5 H | 5 | 1·56 |
| 3 SrO | 156 | 48·60 |
| 11 O | 88 | 27·41 |
| $C^{12}H^5Sr^3O^{14}$ | 321 | 100·00 |

| *Dried cold over oil of vitriol.* | | | Heldt. |
|---|---|---|---|
| 12 C | 72 | 19·67 | 19·27 |
| 10 H | 10 | 2·73 | 2·51 |
| 3 SrO | 156 | 42·63 | 43·61 |
| 16 O | 128 | 34·97 | 34·61 |
| $C^{12}H^{5}Sr^{3}O^{14} + 5Aq$ | 366 | 100·00 | 100·00 |

*b. Bibasic.* — The aqueous acid digested with excess of the salt *a*, and evaporated after filtration, deposits thin, nacreous, crystalline crusts, which, when freed from excess of acid by washing with alcohol, taste neutral, are permanent, give off 8·6 p. c. at 200°, with incipient decomposition, and are insoluble in alcohol. (Heldt.)

| *Crystalline crust.* | | | Heldt. |
|---|---|---|---|
| 12 C | 72 | 23·61 | 24·86 |
| 9 H | 9 | 2·95 | 2·74 |
| 2 SrO | 104 | 34·10 | 34·79 |
| 15 O | 120 | 39·34 | 37·61 |
| $C^{12}H^{6}Sr^{2}O^{14} + 3Aq$ | 305 | 100·00 | 100·00 |

*Citrate of Lime.—Tribasic.*—Citric acid added to an excess of cold lime-water, forms a precipitate only when the solution is nearly saturated, but in presence of a larger quantity of water, only at a boiling heat, and the finely divided crystalline precipitate partially redissolves as the liquid cools. (Heldt.) Tribasic citrate of soda forms with chloride of calcium, a precipitate which dissolves in excess of either of the salts, and is deposited again on evaporating the solution in excess of chloride of calcium. (Berzelius.) The mixture containing excess of chloride of calcium, deposits the whole of the citrate of lime in the crystalline form when boiled; and on being mixed with an additional quantity of citrate of soda and stirred, it suddenly solidifies in the form of a white magma, which becomes crystalline when boiled. (Heldt.) The dilute mixture of the two salts deposits a portion of the citrate of lime in a few weeks, at ordinary temperatures; but on boiling, it immediately deposits the whole, and the salt thus separated does not redissolve on cooling. (H. Rose, *Pogg.* 9, 31.) — The salt dissolves more readily in cold than in hot water, so that the cold solution becomes turbid when boiled. (Heldt.) The salt precipitated from a cold solution dissolves in cold water; but the salt precipitated from a hot solution, which contains less water than the former, is insoluble or nearly so. (Liebig.) The salt dissolves readily in hydrochloric and acetic acid, from which it is precipitated by ammonia only at the boiling heat. The salt dried over oil of vitriol in contact with the air, gives off 12·62 p. c. [4 At.] water at 200°. (Heldt.) — The white powder, which turns litmus blue, putrefies if exposed to the sun in the moist state, giving off hydrogen and carbonic acid, and being converted into carbonate of lime. [For the decomposition in contact with putrefying curd, see page 442.]

| *Dried at* 100°. | | | Berzelius. |
|---|---|---|---|
| 12 C | 72 | 27·91 | |
| 6 H | 6 | 2·32 | |
| 3 CaO | 84 | 32·56 | 32·42 |
| 12 O | 96 | 37·21 | |
| $C^{12}H^{5}Ca^{3}O^{14} + Aq$ | 258 | 100·00 | |

| *Air-dried.* | | | | | | Heldt. |
|---|---|---|---|---|---|---|
| 12 C | 72 | .... | 25·26 | ........ | | 25·21 |
| 9 H | 9 | .... | 3·16 | ........ | | 3·25 |
| 3 CaO | 84 | .... | 29·47 | | | |
| 15 O | 120 | .... | 42·11 | | | |
| $C^{12}H^5Ca^3O^{14}$ + 4 Aq | 285 | .... | 100·00 | | | |

Gay-Lussac & Thénard found in the salt-dried at 100°, 23·27 p.c. C, 4·36 H, 31·17 CaO, and 41·20 O.

*b. Bibasic.* — The solution of the salt *a* in warm citric acid deposits by evaporation, shining laminæ, which taste neutral after washing with alcohol, and after drying in the air, give off 7·3 p. c. (2 At.) water at 150°. (Heldt.) The laminæ, when washed with water, leave a salt similar in composition to the baryta-salt *b*, which no longer dissolves in warm citric acid, and gives off about half its water at 100°. (Berzelius.)

| *Air-dried crystals.* | | | | | Heldt. |
|---|---|---|---|---|---|
| 12 C | 72 | .... | 29·03 | ........ | 29·10 |
| 8 H | 8 | .... | 3·23 | ........ | 3·36 |
| 2 CaO | 56 | .... | 22·58 | ........ | 22·54 |
| 14 O | 112 | .... | 45·16 | ........ | 45·00 |
| $C^{12}H^6Ca^2O^{14}$ + 2Aq.... | 248 | .... | 100·00 | ........ | 100·00 |

*c Monobasic.* — The solution of the salt *a* in excess of acid, leaves on evaporation, a transparent colourless gum, which, when further evaporated, becomes opaquely white and crystalline. (Berzelius.)

The citrates of baryta, strontia, and lime ignited in close vessels, leave pyrophoric residues. (Böttger, *Beiträge,* 2, 44.)

The reaction of lime-water with tribasic or bibasic citrate of potash or soda, is the same as that of baryta-water. (Heldt, p. 448.)

*Citrate of Magnesia.* — *a. Tribasic.* — 1. The acid fully saturated with carbonate of magnesia, deposits in the course of 48 hours, a portion of the salt in the form of a loose powder. (Richter.) The clear saturated solution exposed to a winter temperature, after evaporation, solidifies in a thick magma, (if it has been made with concentrated acid, it solidifies into a hard mass, even without evaporation, according to Delabarre,) and likewise deposits the salt on addition of alcohol. The salt thus precipitated dries up in the air, to a hard pulverulent crust, which gives off 32·0 p. c. (13 At.) water at 150° and 35·43 p. c. (14 At.) at 210°. Crystalline crusts of the same composition are deposited, when a solution not quite saturated with magnesia is evaporated at 50°. (Heldt.) Less bitter than other magnesia salts. (Delabarre, *N. J. Pharm.* 11, 431.) — 2. Tribasic citrate of soda mixed with sulphate of magnesia throws down a white powder (Delabarre); it does not form a precipitate, even when the solutions are highly concentrated. (Heldt.) — [Respecting the preparation of citrate of magnesia see also Wittstein, (*Pharm. Centr.* 1854, 814)].

| *Air-dried crusts.* | | | Heldt. |
|---|---|---|---|
| 12 C | 72 | 20·51 | 20·41 |
| 19 H | 19 | 5·41 | 5·50 |
| 3 MgO | 60 | 17·10 | 17·48 |
| 25 O | 200 | 56·98 | 56·61 |
| $C^{12}H^{5}Mg^{3}O^{14} + 14Aq$ | 351 | 100·00 | 100·00 |

*b. Bibasic.* Gummy mass. (Heldt.) An aqueous solution of bibasic citrate of soda saturated with magnesia, is neutral and yields small crystalline scales when evaporated by heat. (Heldt.)

*Cerous Citrate.* — Alkaline citrates, but not the free acid, throw down from cerous salts a white powder, insoluble in water. Its solution in citric acid leaves when evaporated, a gum from which alcohol extracts the acid, till a neutral salt is left. (Berzelius.)

*Citrate of Yttria.* — *Tribasic.* — Tribasic citrate of soda forms with neutral yttria-salts, a white precipitate, soluble in excess of the yttria salt; this precipitate, after drying in the air, gives off 8·36 p. c. water even below 100°. Its solution in ammonia leaves when evaporated a gum, which dissolves readily in water, does not contain ammonia, and contains the same quantity of yttria as the precipitate. (Berlin.)

*b. Bibasic.* — The solution of *a* in citric acid leaves a gum, which remains transparent even after thorough drying. (Berlin.)

*Citrate of Yttria and Soda.* — Citrate of yttria dissolves abundantly in aqueous citrate of soda. The solution when evaporated, leaves a gum which dissolves readily in water; it is not precipitated by ammonia, potash, soda, carbonate of soda, or oxalate of ammonia, but yields a precipitate with acid oxalate of potash. (Berlin.)

*Citrate of Glucina.* — Soluble gum. (Vauquelin.)

*Citrate of Alumina.* — Insoluble powder when it contains excess of alumina; soluble gum, when the acid is in excess. (Richter.)

*Citrate of Thorina.* — When hydrate of thorina is digested with citric acid, a *neutral* salt is formed, which remains undissolved in white flakes; and a solution of the *acid* salt, which, without yielding crystals, dries up to sour-tasting syrup. Both salts dissolve readily in alcohol, and then yield by evaporation a transparent gum, soluble in water. (Berzelius.)

*Citrate of Zirconia.* — Soluble, inasmuch as alkaline citrates do not precipitate zirconia-salts. (Berzelius.)

Recently precipitated hydrate of tantalic acid dissolves in citric acid, according to Wollaston; but, according to Gahn, Berzelius & Eggertz, it is nearly if not quite insoluble in that acid.

*Vanadic Citrate.* — The blue solution dries up to a bluish black amorphous mass, which redissolves slowly in cold water, forming a dark blue solution, and forms with ammonia a dark brownish-yellow solution,

which, when exposed to the air, is quickly decolorised, in consequence of the formation of vanadic acid. (Berzelius.)

*Chromous Citrate.* — Protochloride of chromium forms with tribasic citrate of soda, a violet-red precipitate, which dissolves slowly in the cold, more quickly when heated, forming a dark green liquid. (Moberg, *J. pr. chem.* 44, 330.)

*Chromic Citrate.* — The aqueous solution, which exhibits a reddish colour by transmitted light, yields pale green crystals by evaporation. (Brandenburg.) The evaporated mass splits up into thin sticks. (Hayes.)
Bichromate of potash treated with citric acid yields *chromocitrate of potash*, $C^{12}H^6,Cr^2O^3,O^{12}+KO+3HO$, $[= C^{12}H^6(Cr^2O^2)KO^{14} + 3\,Aq]$, in which the potash may be replaced by other bases. (Malaguti, *Compt. rend.* 16, 457.)

*Uranic Citrate.* — Very pale yellow, slightly soluble in water. (Richter.)

*Manganous Citrate.* — *Bibasic.* — Carbonate of manganese digested with a slight excess of the acid, yields a solution which deposits by evaporation, a white, heavy, tasteless crystalline powder. The air-dried salt remains unaltered at 150°, but gives off 6·86 p.c. (2 At.) water at 220°. It is insoluble in water, dissolves readily in hydrochloric, sparingly in acetic acid. Its solution in bibasic citrate of soda dries up to a gum. (Heldt.)

| *Air-dried.* | | | Heldt. |
|---|---|---|---|
| 12 C | 72 | 27·27 | 27·68 |
| 8 H | 8 | 3·03 | 3·17 |
| 2 MnO | 72 | 27·27 | 27·16 |
| 14 O | 112 | 42·43 | 41·99 |
| $C^{12}H^6Mn^2O^{14} + 2Aq$ | 264 | 100·00 | 100·00 |

*Potassio-antimonic Citrate.* — 1 pt. of citric acid is neutralised with potash, 1 pt. more of the acid added, the mixture boiled for some time with teroxide of antimony, and the filtrate left to crystallise. White, shining, very hard prisms grouped in tufts. They give off 6·69 p.c. (5 At.) water at 190°. The aqueous solution of the salt is not readily decomposed by acids; with nitrate of silver, it forms a precipitate, in which the potash is replaced by oxide of silver; it contains however 1 At. acid and 2 At. oxide of silver to 1 At. antimonic oxide. (Thaulow, *Ann. Pharm.* 27, 334.)

| *Dried at* 190°. | | | Thaulow. |
|---|---|---|---|
| 24 C | 144·0 | 23·06 | 23·41 |
| 10 H | 10·0 | 1·60 | 1·85 |
| 3 KO | 141·6 | 22·67 | 22·38 |
| $SbO^3$ | 153·0 | 24·49 | 24·08 |
| 22 O | 176·0 | 28·18 | 28·28 |
| $C^{12}H^5K^3O^{14},C^{12}H^5SbO^{14}$ | 624·6 | 100·00 | 100·00 |

| *Air-dried crystals.* | | | Thaulow. |
|---|---|---|---|
| 24 C | 144·0 | 21·50 | 21·70 |
| 15 H | 15·0 | 2·24 | 2·31 |
| 3 KO | 141·6 | 21·15 | 21·06 |
| $SbO^3$ | 153·0 | 22·85 | 22·69 |
| 27 O | 216·0 | 32·26 | 32·24 |
| $C^{12}H^5K^3O^{14},C^{12}H^5SbO^{14} + 5Aq.$ | 669·6 | 100·00 | 100·00 |

*Telluric Citrate.* — The solution of hydrated telluric oxide in the acid yields by spontaneous evaporation, large transparent, colourless prisms, easily soluble in water. (Berzelius.)

*Citrate of Zinc.* — *Tribasic.* — Precipitated on saturating the dilute acid with the metal, the oxide or the carbonate, and evaporating by heat, as a white, heavy, crystalline granular powder (Scheele, Heldt), or in small shining tables having a harsh metallic taste. (Vauquelin.) The salt does not lose weight at 100° (Heldt); when ignited in a close vessel, it leaves a pitch-black powder, which burns in the air with a glimmering light, when touched by burning tinder (Böttger); it dissolves in 100° pts. of cold and in a smaller quantity of hot water (Vauquelin) forming a liquid which is precipitated by sulphuretted hydrogen. (Heldt.)

| *Dried at* 100°. | | | Heldt. |
|---|---|---|---|
| 12 C | 72·0 | 23·71 | 23·94 |
| 7 H | 7·0 | 2·31 | 2·34 |
| 3 ZnO | 120·6 | 39·72 | 39·42 |
| 13 O | 104·0 | 34·26 | 34·30 |
| $C^{12}H^5Zn^3O^{14} + 2Aq$ | 303·6 | 100·00 | 100·00 |

*b.* 5 *At. Base to* 2 *At. Acid.* — The aqueous solution of the salt *a*, mixed with a small quantity of citric acid, deposits transparent crystals when evaporated at a gentle heat. (Heldt.)

| *Air-dried crystals.* | | | Heldt. |
|---|---|---|---|
| 24 C | 144 | 25·81 | 25·76 |
| 13 H | 13 | 2·33 | 2·40 |
| 5 ZnO | 201 | 36·02 | 35·74 |
| 25 O | 200 | 35·84 | 36·10 |
| $C^{12}H^5Zn^3O^{14},C^{12}H^6Zn^2O^{14} + 2Aq$ | 558 | 100·00 | 100·00 |

Bibasic citrate of *soda* dissolves carbonate of *zinc*, forming a neutral liquid, which when left to evaporate, is completely converted into small shining crystalline laminæ, permanent in the air. (Heldt.) — The hydrate precipitated from sulphate of zinc by ammonia dissolves in aqueous terbasic citrate of *potash*, forming an alkaline liquid. (Schmidt, *Mag. Pharm.* 13, 68.)

*Citrate of Cadmium.* — The aqueous acid dissolves the metal sparingly, the carbonate readily. White granular powder nearly insoluble in water. (Stromeyer.)

*Citrate of Lead.* — *a. Sexbasic.* — The salt *d*, pressed after precipitation, but still moist, is digested for 12 hours with basic acetate of lead, the powder washed with water, after the liquid has been decanted, and dried at 100° in a current of air (Berzelius); or in cold air over oil of vitriol. (Heldt.) White, non-crystalline powder, insoluble in water. (Heldt.)

| *Dried.* | | | Berzelius. | Heldt. |
|---|---|---|---|---|
| 12 C | 72 | 8·51 | | 8·59 |
| 6 H | 6 | 0·71 | | 1·06 |
| 6 PbO | 672 | 79·43 | 77·60 | 79·03 |
| 12 O | 96 | 11·35 | | 11·32 |
| $3PbO,C^{12}H^5Pb^3O^{14} + Aq$ | 846 | 100·00 | | 100·00 |

*b. Quintobasic.* — Obtained by digesting the salt *d* with ammonia, out of contact with the air. White, bulky powder, insoluble in water. After drying in cold air over oil of vitriol, it gives off 3·37 p.c. (3 At.) water at 100°. (Heldt.)

| | | | Heldt. |
|---|---|---|---|
| 12 C | 72 | 9·58 | 9·52 |
| 8 H | 8 | 1·06 | 1·06 |
| 5 PbO | 560 | 74·47 | 74·34 |
| 14 O | 112 | 14·89 | 15·08 |
| $2PbO,C^{12}H^5Pb^3O^{14} + 3Aq$ | 752 | 100·00 | 100·00 |

*c. Quadrobasic.* — The moist salt *d* is digested for 24 hours in a close vessel at 60°, with water containing a small quantity of ammonia (a larger quantity would dissolve the whole) and the powder dried at 100° in dry air, after the liquid, which contains an ammoniacal double salt, has been decanted. It contains 71·33 p. c. oxide of lead. (Berzelius.)

*d. Tribasic.* 1. Aqueous neutral acetate of lead in excess is precipitated by citric acid. The precipitate contains a small quantity of acetate of lead, from which it may be freed by continued washing, but at the same time it becomes continually more basic, in consequence of the abstraction of the acid citrates. (Berzelius.) — 2. Better: An alcoholic solution of neutral acetate of lead is precipitated by alcoholic citric acid, and washed with alcohol, as long as the alcohol extracts any lead. (Berzelius.) — 3. Neutral acetate or nitrate of lead (which is not precipitated by free citric acid) is precipitated by citrate of soda, an excess of which however redissolves the precipitate. — Citrate of ammonia precipitates nitrate of lead, at least when evaporated with it. The precipitate obtained by (2) becomes continually more basic by washing with water, so that its amount of lead rises to 69 per cent., and even higher. (Berzelius.) — White powder (Berzelius) somewhat granular when precipitated from a hot solution, though it retains the same composition. (Heldt.) After drying in the air, it gives off 1·44 p.c. (1 At.) water at 120°. (Heldt.) It dissolves readily in nitric acid and ammonia, also in citrate of soda. (Berzelius.) It dissolves completely in hot hydrochlorate, nitrate, and succinate of ammonia, and with turbidity in carbonate of ammonia. (Wittstein.)

| | | | Berzelius. *Ann. Chim.* 94, 170. | *Pogg.* 27, 282. | Heldt. |
|---|---|---|---|---|---|
| 12 C | 72 | 14·12 | 14·14 | 12·80 | 13·99 |
| 6 H | 6 | 1·18 | 1·30 | 1·02 | 1·25 |
| 3 PbO | 336 | 65 88 | 65·82 | 69·00 | 65·79 |
| 12 O | 96 | 18·82 | 18·74 | 17·18 | 18·97 |
| $C^{12}H^5Pb^3O^{14}$ + Aq | 510 | 100·00 | 100·00 | 100·00 | 100·00 |

The second salt analysed by Berzelius had become basic by continued washing.

*e. 5 At. base to* 2 *At. acid.* — Remains in the form of a white, heavy, crystalline powder, when the salt *d* is treated with concentrated citric acid, then washed with water, and dried cold over oil of vitriol. (Heldt.)

| *Dried over oil of vitriol.* | | | Heldt. |
|---|---|---|---|
| 24 C | 144 | 15·86 | 16·30 |
| 12 H | 12 | 1·32 | 1·58 |
| 5 PbO | 560 | 61·67 | 60·98 |
| 24 O | 192 | 21·15 | 21·14 |
| $C^{12}H^5Pb^3O^{14},C^{12}H^6Pb^2O^{14}$ + Aq | 908 | 100·00 | 100·00 |

*b. Bibasic.* — 1. A boiling aqueous solution of neutral acetate of lead is added by small portions to boiling aqueous citric acid, till the precipitate, which at first continually redissolves, begins to become permanent; the liquid decanted from this precipitate is then left to cool slowly till it crystallises. — 2. The salt *d* is digested with aqueous citric acid, the solution decanted (from the salt *e*, according to Heldt), and cooled. (Berzelius.) — 3. Boiling very dilute nitric acid is saturated with the salt *d*, the solution decanted and left to cool, and the mother-liquor which is poured off from the crystals, saturated at the boiling heat with the salt *d*. (Berzelius.) The crystals obtained by (3) are long prisms and always contain nitrate of lead. (Heldt.)—Granular and laminar crystals. They do not give off any thing at 120°. (Berzelius.) At 170°, they turn brownish-yellow and give off 8·35 per cent. (Heldt.) They bake together when heated in an open crucible, swell up at about 180° without turning brown, and ultimately leaving a residue consisting chiefly of reduced lead. When heated with oxide of lead, they give off 4·78 p. c. water. They are gradually decomposed by water (and dissolve in it, according to Heldt). They dissolve in ammonia. (Berzelius.)

| | | | Berzelius. | Heldt. |
|---|---|---|---|---|
| 12 C | 72 | 17·31 | | 17·07 |
| 8 H | 8 | 1·92 | | 2·16 |
| 2 PbO | 224 | 53·85 | 53·63 | |
| 14 O | 112 | 26·92 | | |
| $C^{12}H^6Pb^2O^{14}$ + 2Aq | 416 | 100·00 | | |

Oxide of lead will not combine with a larger proportion of citric acid. (Berzelius.)

*Ammonio-citrate of Lead.* — The solution of the salt *d* in ammonia leaves, when evaporated, a yellowish soluble gum which does not give off its ammonia even in vacuo. The solution of salt in ammonia is reduced

by spontaneous evaporation to a jelly, which dries up to a gum with white efflorescences on the edge; on redissolving it in water, an ammoniacal salt remains in scales having a mother-of-pearl lustre, like a solution of soap. (Berzelius.)

The salt *d* dissolves in aqueous *tribasic citrate of soda,* forming a double salt. (Berzelius.)

*Ferrous Citrate.* — The aqueous acid dissolves iron, with evolution of hydrogen, and forms a brown liquid, which does not yield crystals, and is not precipitated by potash, inasmuch as citrate of potash dissolves ferric oxide. (Scheele.) From the saturated pale yellow iron-solution, alcohol throws down the salt in white flakes, which shrink together at the bottom and turn brown. (Heldt.) The iron-solution yields by evaporation a white powder which has an inky taste and oxidises in damp air. (Béral, *J. Chim. méd.* 16, 604.)

The solution of magnetic oxide of iron in citric acid, leaves when evaporated, green, transparent amorphous laminæ, which do not turn brown on exposure to the air. (Béral.)

*Ferric Citrate.* — The red-brown sweetish solution obtained by saturating warm aqueous citric acid with recently precipitated ferric hydrate, dries up to a syrup by spontaneous evaporation, and afterwards in the water-bath to a mass, which is brittle in the cold, flexible when warmed, easily soluble in water (Vauquelin); to a specular film having the metallic lustre and exhibiting in thin films a light-brown colour (garnet-red, according to Duvivier, *J. Chim. méd.* 18, 638) by transmitted light. (Heldt.) It contains 32·1 p.c. water at 100°. (Duvivier.) From the aqueous solution, alcohol throws down the red-brown salt; potash and carbonate of potash, the sesquioxide; and ferrocyanide of potassium, Prussian blue. (Heldt.) The yellow solution of ferric hydrate in citric acid, leaves when evaporated below 50°, a brownish-yellow, somewhat transparent, resinous mass, which yields a cinnamon-coloured powder, has a slight sweetish ferruginous taste, contains 29·5 p.c. ferric oxide, becomes slightly moist when exposed to the air, chars when heated, without fusion or tumefaction, and dissolves completely in water. The solution is completely precipitated by cold potash; but with carbonate of potash, it forms in the cold a clear dark-coloured mixture, and is only precipitated when heated. When the solution is boiled, part of the sesquioxide is reduced to protoxide, but much less quickly and in smaller quantity than in the case of tartaric acid. The dry salt is insoluble in boiling 90 per cent. alcohol, sparingly, and with yellow colour in alcohol of 40 to 20 per cent. (Wittstein, *Repert.* 92, 1.)

Ferrocyanide of potassium does not precipitate an acid solution of ferric citrate, but forms a blue liquid, which is decolorised by ammonia. (Callond, x, 315.) — Citric acid prevents the precipitation of sesquichloride of iron by alkalis. (H. Rose.)

*Ammonio-ferric Citrate.* — 23 pts. of dry ferric citrate and 10 pts. of crystallised citric acid are dissolved in water, neutralised with ammonia, and the solution evaporated to dryness at a gentle heat. (Haidlen, *Repert.* 84, 391); or 2 pts. of recently precipitated ferric hydrate are dissolved in 3 pts. of citric acid, the solution saturated with ammonia, and evaporated. (Wittstein.) — The yellowish-brown, shining, brittle, amorphous mass,

has a slightly saline ferruginous taste, contains 10 p. c. ferric oxide, becomes slowly moist in the air, and dissolves in water, but is nearly insoluble in alcohol. (Haidlen.) — The greenish-yellow mass contains 20 per cent. ferric oxide and 8 p. c. ammonia; does not melt when heated, but swells up slightly and leaves a large quantity of charcoal; dries up to an extract by exposure to the air; and forms with water a greenish-yellow solution in which no protoxide of iron is formed, even after long boiling, but the whole of the sesquioxide is precipitated by cold potash; the same solution becomes dark yellow when mixed with carbonate of potash, and deep brown when heated, but deposits the greater part of the oxide only after long boiling. The greenish-yellow mass is insoluble in strong alcohol, but dissolves with tolerable facility in alcohol of 40 p. c. forming a greenish-yellow solution. (Wittstein.) — Ferric citrate dissolves, with rise of temperature and incipient agglutination, in an equal quantity of ammonia and half as much water, forming a dark-red liquid, which, when evaporated at a gentle heat in shallow basins, gives off the greater part of the ammonia and leaves dark garnet-coloured scales. These scales still contain ammonia, but do not weigh much more than the original ferric citrate. They have a slight taste, which is more agreeable as the acid is more saturated with ferric oxide. They give off their ammonia at a gentle heat without fusion or tumefaction, and leave black scales no longer soluble in water. They deliquesce in the air, dissolve with red colour in any quantity of water, but not in strong alcohol, which indeed partly precipitates the salt from its aqueous solution. (Depaire, *N. J. Pharm.* 16, 90.)

*Sodio-ferric Citrate.* — The red-brown solution of recently precipitated ferric hydrate in bibasic citrate of soda, dries up by evaporation to a light-brown specular film, having a metallic lustre and deliquescing in the air. (Heldt.)

*Citrate of Cobalt.* — *Tribasic.* — The dark-red solution of carbonate of cobalt in the warm acid solidifies on cooling, after sufficient evaporation, forming a light rose-coloured magma which dries up to a powder of the same colour. When dried over the water-bath, it leaves a light coloured shining opaque specular film. The powder gives off 9·3 p. c. (4 At.) water at 100°, and assumes a light violet colour; becomes dark violet at 220°, and gives off 31·4 p. c. (4 At.) water in all; and afterwards dissolves completely in water in the form of the original solution. From the aqueous solution, the salt is precipitated by alcohol; ammonia dissolves it clearly; potash precipitates it dark blue; and carbonate of potash, violet, but only when heated. (Heldt.)

| *Dried in cold air over oil of vitriol.* | | | Heldt. |
|---|---|---|---|
| 12 C | 72·0 | 17·84 | 18·10 |
| 19 H | 19·0 | 4·71 | 4·70 |
| 3 CoO | 112·5 | 27·88 | 27·76 |
| 25 O | 200·0 | 49·57 | 49·44 |
| $C^{12}H^{5}Co^{3}O^{14} + 14Aq$ | 403·5 | 100·00 | 100·00 |

The *bibasic* and *monobasic* salts yield no crystals, but when evaporated over the water-bath, leave dark-red, shining films. (Heldt.)

The dark-red neutral solution of carbonate of cobalt in bibasic citrate of soda dries up to an amorphous gum. (Heldt.)

*Citrate of Nickel.* — *Tribasic.* — The green, sweet-tasting solution of oxide of nickel in the acid solidifies in a green pulp by spontaneous evaporation, and, when evaporated at a gentle heat, leaves an olive-green shining film which yields a light-green powder. The air-dried salt gives off 23·7 p.c. (11 At.) water at 100°, and 30·99 p. c. (14 At.) at 200.° It is precipitated from its aqueous solution by alcohol. Potash and carbonate of potash precipitate the solution only on boiling, and ammonia turns it blue without precipitation. (Heldt.) Tupputi obtained the salt in greenish-white flakes soluble in acids.

| *Dried in cold air over oil of vitriol.* | | | Heldt. |
|---|---|---|---|
| 12 C | 72·0 | 17·84 | 17·70 |
| 19 H | 19·0 | 4·71 | 4·81 |
| 3 NiO | 112·5 | 27·88 | 27·52 |
| 25 O | 200·0 | 49·57 | 49·97 |
| $C^{12}H^5Ni^3O^{14} + 14Aq$ | 403·5 | 100·00 | 100·00 |

The bibasic and monobasic citrates of nickel, and the double salt which it forms with soda, resemble the corresponding salts of cobalt. (Heldt.)

*Cupric Citrate.* — *Quadrobasic.* The solution of cupric carbonate in citric acid (or the mixture of cupric acetate with the acid, according to Jul. Gay-Lussac), deposits on boiling, a green crystalline powder composed of microscopic rhombohedrons. Citrate of soda does not precipitate cupric acetate at the boiling heat. The precipitate gives off 5·4 p. c. (2 At.) water at 100°, assuming an azure-blue colour, and decomposes at 170°. Its blue solution in ammonia becomes turbid when mixed with alcohol, and gradually deposits oily drops which do not solidify even after long standing. (Heldt.)

| *Dried in cold air over oil of vitriol.* | | | Heldt. |
|---|---|---|---|
| 12 C | 72 | 20·45 | 20·63 |
| 8 H | 8 | 2·27 | 2·39 |
| 4 CuO | 160 | 45·46 | 45·46 |
| 14 O | 112 | 31·82 | 31·52 |
| $CuO,C^{12}H^5Cu^3O^{14} + 3Aq$ | 352 | 100·00 | 100·00 |

According to Jul. Guy-Lussac (*Ann. Pharm.* 5, 135), the salt contains 4 Aq.

*Mercurous Citrate.* — From mercurous acetate, but not from the nitrate, citric acid precipitates a white powder, soluble in nitric acid. (Scheele.) The solution of mercurous oxide in warm citric acid deposits, on cooling, a mixture of mercurous and mercuric salt, in the form of a white powder. (Burckhardt.) By triturating the crystals of citrate of soda and mercurous nitrate with water, a white salt is obtained, which becomes greyish by the action of cold, and still more by that of boiling water, to which it gives up both mercurous and mercuric salt, whilst a portion of the mercurous salt remains undissolved together with metallic

mercury. (H. Rose, *Pogg.* 53, 127.) — The white, metallic-tasting powder obtained by precipitating mercurous nitrate with citrate of potash, contains after washing and drying, 50·89 p. c. mercurous oxide (70·75 p. c. according to Harff); blackens when exposed to light, turns yellow when heated, and finally leaves a porous-charcoal; it is decomposed with fire, by potassium, and dissolves readily in nitric, citric, and acetic acid, as well as in oil of vitriol, and does not blacken when boiled with oil of vitriol. (Burckhardt, *N. Br. Arch.* 11, 265.)

*Ammonio-mercurous Citrate.* — Ammonia forms with mercurous citrate suspended in water, a black powder, which contains 87·98 p. c. mercurous oxide; gives off ammonia when treated with potash, and is insoluble in water, but dissolves in acetic acid, leaving only a few globules of mercury. (Harff. *N. Br. Arch.* 5, 279.)

*Mercuric Citrate.* — The solution of mercuric oxide in boiling citric acid deposits, on cooling, a white powder, (crystalline, according to Harff), which contains 35·81 per cent. of mercuric oxide; does not blacken by exposure to light; dissolves sparingly in water, and only at the boiling heat, swelling up at the same time like a jelly; but is easily dissolved by nitric, acetic, and citric acid, and by warm citrate of potash. (Burckhardt.) It is also precipitated by citrate of potash from mercuric nitrate, but is then a white flocculent powder containing 63·98 p. c. mercuric oxide. (Harff, *N. Br. Arch.* 5, 279.)

*Ammonio-mercuric citrate.* — *a. Basic.* — The following salt *b* (or the preceding salt according to Harff) dissolved in a large quantity of water, forms with ammonia a white powder which (according to Harff, contains 79·71 p. c. mercuric oxide, and turns yellow and gives off ammonia, when treated with potash) is insoluble in water, and dissolves only in strong boiling nitric acid (readily in hydrochloric and nitric acid, according to Harff), likewise in ammonia, and in nitrate and citrate of ammonia. (Burckhardt.) — *b. Neutral.* — The solution of mercuric citrate in warm citrate solidifies, after evaporation, in the form of a translucent jelly, which dries up with difficulty over the water-bath, deliquesces in the air, and dissolves in water, with separation of a basic salt, but completely in nitric acid. (Burckhardt.)

*Argentous Citrate.* — *Citrate of Suboxide of Silver.* — When hydrogen gas is passed over argentic citrate, water is formed, and the salt is rapidly converted into a dark-brown mixture of the argentous salt and free citric acid. If the free acid be dissolved out by water, till the water acquires a dark wine-red colour by dissolving the argentous salt, and the residue be then dried, the argentous citrate is obtained in the separate state. This salt detonates when heated, less strongly than the argentic salt, and leaves 76 p. c. silver; whence its composition is $Ag^2O,C^4H^2O^4$. [or $C^{12}H^5Ag^6O^{14}$,Aq.] It dissolves slowly in water; the deep red solution, when boiled, gives off a small quantity of gas, assumes a colour between yellow-green and blue, likewise exhibiting iridescence, but afterwards loses its colour and deposits metallic silver; the red solution mixed with potash, is decolorized, and yields a black precipitate (vi, 139). The deep red-yellow solution of the argentous salt in ammonia, is decomposed by boiling in a similar manner to the aqueous solution, and often deposits a

golden-yellow specular film, which exhibits a green translucence, and is reduced to white silver when heated. (Wöhler, *Ann. Pharm.* 30, 2.)

*Argentic Citrate; Citrate of Silver.* — *Tribasic.* — 1. The acid forms with protoxide of silver, a white, metallic-tasting, insoluble powder, which is blackened by light; it contains 64 p. c. oxide of silver, and when subjected to dry distillation, gives off very strong (somewhat empyreumatic) acetic acid, and leaves arborescent silver mixed with charcoal. (Vauquelin.) — 2. Citrate of potash, even the acid citrate (Liebig), but not the free acid (Vauquelin), added to nitrate of silver, throws down the tribasic salt in the form of a white powder. — According to Liebig and Dumas, (*N. Ann. Chim. Phys.* 5, 358; also *Ann. Pharm.* 44, 73,) it is $C^{12}H^5Ag^3O^{14}$; according to Berzelius, $AgO,C^4H^2O^4[=C^{12}H^5Ag^3O^{14}+Aq]$. When, however, the mixture is heated to 60°, the precipitate changes very quickly, and with loss of water, into a heavy crystalline powder, and the same change takes place slowly in the cold; hence, to obtain the precipitate for the most part unaltered, and composed of AgO, $C^4H^2O^4$, it must be quickly washed with cold water, dried between paper frequently renewed, and finally in a cold vacuum, because it gives off water between 60° and 100°. But the precipitate, after being converted into a heavy powder, is a mixture of 1 At. aconitate and 2 At. citrate of silver; $AgO,C^4HO^3+2(AgO,C^4H^2O^4)$; hence by shaking it up with strong alcohol and a very small quantity of fuming hydrochloric acid, and evaporating the filtrate, which should no longer form a cloud with solution of nitrate of silver a colourless residue is obtained, whose aqueous solution no longer crystallizes, and whose compound with soda yields crystals of citrate of soda, but at the same time, a mother liquor, containing an uncrystallisable salt, which dissolves in alcohol. (Berzelius, *vid.* p. 444.) — The salt does not give off anything at 120°. If it has been dried without pressure, it takes fire when touched by a glowing body, and burns quietly away like amadou. When heated in the mass, it detonates slightly, and leaves light flocks of silver, which unite together at a stronger heat. The salt dissolves in boiling water, and yields on cooling concentric white or yellowish needles. (Liebig.)

| *At* 100°. | | | Liebig. | Jul. Guy-Lussac. | Dumas. |
|---|---|---|---|---|---|
| 12 C | 72 | 14·04 | 13·96 | | 14·05 |
| 5 H | 5 | 0·97 | 0·98 | | 1·05 |
| 3 Ag | 324 | 63·16 | 62·98 | 62·15 | 62·65 |
| 14 O | 112 | 21·83 | 22·08 | | 22·25 |
| $C^{12}H^5Ag^3O^{14}$ | 513 | 100·00 | 100·00 | | 100·00 |

*Citrate of Silver and Calcium.* — Obtained by precipitating tribasic citrate of lime, dissolved in a large quantity of water, with nitrate of silver. (White, Chodnew, *Ann. Pharm.* 53, 283.)

| | | | Chodnew. |
|---|---|---|---|
| 12 C | 72 | 15·89 | 15·50 |
| 5 H | 5 | 1·10 | 1·26 |
| 2 AgO | 232 | 51·21 | 50·60 |
| 2 CaO | 56 | 12·37 | 13·15 |
| 11 O | 88 | 19·43 | 19·49 |
| $CaO,C^{12}H^5Ag^2CaO^{14}$ | 453 | 100·00 | 100·00 |

*Citrate of Palladium.* — Alkaline citrates form a light yellow precipitate with nitrate of palladium. (Berzelius.)

Citric acid dissolves readily in *alcohol*, but not so readily as in water.

In *ether* it dissolves very readily and abundantly, both in the crystalline and in the fused state; on evaporating the solution, there remains a syrup, which scarcely reddens dry litmus-paper, and when left in contact with the air, is converted into the ordinary crystals. (Wackenrode.)

In boiling *creosote* it dissolves so abundantly, that the solution solidifies on cooling. (Reichenbach.)

¶ *Citrate of Aniline.* — An alcoholic solution of 1 At. citric acid mixed with 1 At. aniline containing a small quantity of water, dries up, in vacuo over oil of vitriol, to a viscid brown-red mass, in which crystals begin to appear after a while, and ultimately fill the entire mass. This crystalline product is triturated with a small quantity of alcohol, the liquid squeezed out through linen, the residue dissolved in strong alcohol, and the solution left over oil of vitriol till it crystallises. — Slender needles united in rounded groups, melting at a temperature a little below 100°, very soluble in alcohol, and still more in water.

| *Dried over oil of vitriol.* | | | Pebal. |
|---|---|---|---|
| 24 C | 144 | 50·53 | 50·61 |
| N | 14 | 4·91 | |
| 15 H | 15 | 5·26 | 5·46 |
| 14 O | 112 | 39·30 | |
| $C^{12}NH^7,C^{12}H^8O^1$ | 285 | 100·00 | |

The salt heated to a temperature between 140° and 150°, gives off water and yields citranilic acid (p. 465).

The bibasic and tribasic citrates of aniline do not appear to crystallise. (Pebal, *Ann. Pharm.* 82, 91.) ¶.

## *Conjugated Compounds of Citric Acid.*

## Tribasic Citrate of Methyl.

$$C^{18}H^{14}O^{14} = 3C^2H^3O,C^{12}H^5O^{11}.$$

St. Evre (1845). *Compt. rend.* 21, 1441; also *J. pr. Chem.* 37, 437.

*Dritel-Citronformester.*

A solution of citric acid in wood-spirit saturated with dry hydrochloric acid gas, is gradually heated to 90°, whereupon the liquid assumes a yellow colour, and wood-spirit and chloride of methyl are expelled. The mixture, after standing for 24 hours, deposits prismatic crystals, which must be collected, pressed between paper, and dried in vacuo. (St. Evre.)

| | | | |
|---|---|---|---|
| 18 C | 108 | 46·16 | 45·93 |
| 14 H | 14 | 5·98 | 5·87 |
| 14 O | 112 | 47·86 | 48·20 |
| $C^{18}H^{14}O^{14}$ | 234 | 100·00 | 100·00 |

## Bibasic Citrate of Methyl? or Bimethylocitric Acid.?

$C^{16}H^{12}O^{14} = 2C^2H^3O,HO,C^{12}H^5O^{11}$.

The mother-liquor of the above-mentioned crystals. (St. Evre.)

| | | | St. Evre. |
|---|---|---|---|
| 16 C | 96 | 43·64 | 42·56 |
| 12 H | 12 | 5·45 | 6·18 |
| 14 O | 112 | 50·91 | 51·26 |
| $C^{16}H^{12}O^{14}$ | 220 | 100·00 | 100·00 |

*Bimethylocitrate of Lime* dissolves very easily in water and in alcohol, (Demondesir.)

*Monomethylocitric Acid*, $C^2H^3O,2HO,C^{12}H^5O^{11}$, is also formed, together with the preceding compounds, by the action of hydrochloric acid gas on citric acid dissolved in wood-spirit. Its *lime-salt* dissolves very easily in water, but is insoluble in alcohol. (Demondesir, *Compt. rend.* 33, 227.)

## Tribasic Citrate of Ethyl.

$C^{24}H^{20}O^{14} = 3C^4H^5O,C^{12}H^5O^{11}$.

THENARD. *Mém de la Soc. d'Arcueil*, 2, 12.
MALAGUTI. *Ann. Chim. Phys.* 63, 197; also *Ann. Pharm.* 21, 267; also *J. pr. Chem.* 11, 279.
HELDT. *Ann. Pharm.* 47, 195.

*Citric ether.*

*Preparation.* — 15 pts. of citric acid are distilled with 18 pts. of alcohol and 5 pts. of oil of vitriol, till vinic ether begins to pass over; the residue in the retort, mixed with water after cooling, and the citric ether thereby precipitated, washed with dilute potash, and afterwards with water. (Thénard.) — 2. Nine parts of crystallised citric acid reduced to powder are introduced into a tubulated retort, together with 11 pts. of alcohol of sp. gr. 0·814; 5 pts. of oil of vitriol then gradually added; the mixture gradually heated and boiled, till about $\frac{1}{3}$ of the alcohol has passed over, and vinic ether is evolved in perceptible quantity; the residue in the retort decanted after cooling, and mixed with twice its volume of water; the citric ether, which immediately sinks to the bottom, washed several times, first with pure water, then with water containing potash, then again with pure water, till the wash-water evaporates without residue;

the washed residue dissolved in alcohol; the solution decolorised by digestion with very pure animal charcoal, and the filtrate finally evaporated in vacuo. 100 pts. of citric acid thus treated, yield 6 pts. of citric ether. (Malaguti.) — When a mixture of 1 pt. oil of vitriol, 2 pts. citric acid, and 3 pts. alcohol, is distilled for four hours, with cohobation, whereupon scarcely anything distils over but vinic ether, and a small quantity of alcohol; — the very dark-brown residue mixed with water; the precipitated dark-brown citric ether washed with water, and decolorised with animal charcoal: it appears yellowish, boils at 230°, may be distilled without decomposition, and contains 56·13 p. c. C, 6·96 H, and 36·91 O, which is the composition of aconitic ether (p. 408). By still further distillation and cohobation of the above-mentioned mixture, an ether is obtained, which contains 57·78 p. c. C, 7·27 H, and 35·05 O, and therefore resembles citraconic ether(x, 423,) in composition. (Marchand, *J. pr. Chem.* 20. 318.) — 3. Boiling absolute alcohol is saturated with citric acid, then, likewise at the boiling heat, with dry hydrochloric acid gas; the greater part of the hydrochloric acid, together with chloride of ethyl, removed by evaporation; and the residual ether washed several times with very dilute carbonate of soda, then with water, evaporated over the water-bath, and set aside for a week over chloride of calcium. (Heldt.) Demondesir (*Compt. rend.* 33, 227), saturates an alcoholic solution of citric acid with hydrochloric acid gas, neutralizes the acid liquor with an alkaline carbonate, shakes it up several times with vinic ether to dissolve the citric ether, and obtains the latter in the free state by evaporation. By this process, 5 pts. of citric acid yield 4 pts. of citric ether. — When fused citric acid is mixed with alcohol, as in the preparation of oxalic ether (ix, 179, 3), an ether is likewise obtained, which may, however, be aconitic or citraconic ether. (Gaultier de Claubry.)

*Properties.* — Yellowish oil (Thénard, Malaguti), transparent, of sp. gr. 1·142 at 21°. (Malaguti.) Not volatile (Thénard); distils with partial decomposition (Malaguti). Inodorous (Thénard); has a faint odour like that of olive-oil (Malaguti); very bitter. (Thénard, Malaguti.) Neutral. (Malaguti.)

| | | | Dumas. | Malaguti. | Heldt. |
|---|---|---|---|---|---|
| 24 C | 144 | 52·17 | 52·3 | 51·05 | 50·65 |
| 20 H | 20 | 7·25 | 7·2 | 7·29 | 7·40 |
| 14 O | 112 | 40·58 | 40·5 | 41·66 | 41·95 |
| $C^{24}H^{20}O^{14}$ | 276 | 100·00 | 100·0 | 100·00 | 100·00 |

The above result was obtained by Dumas (*Compt. rend.* 8, 528; also *Ann. Pharm.* 30, 91; also *J. pr. Chem.* 17, 18) in three analyses of the ether, the preparation of which however he does not describe. Whether Malaguti and Heldt examined the same ether, only not completely dehydrated, or a distinct compound $C^{24}H^{10}O^{15}$, there is no means of deciding.

*Decompositions.* 1. Citric ether becomes reddish at 270°, and boils with partial decomposition at 283°, yielding a brown oil, then water containing alcohol, and at last citric ether, together with a gas containing carbon, and leaves a residue of charcoal. — 2. When heated in an open vessel it gives off dense inflammable vapours, and leaves charcoal. — 3. Its solution in nitric acid, when gently heated, gives off red fumes, acquires the odour of nitrous ether, and after continued boiling, leaves a yellow residue, which contains oxalic acid, and turns red when treated with ammonia. — 4. Its solution in oil of vitriol begins to decompose at 70°, gives off vinic ether and alcohol at a higher temperature, and leaves a

clear, red, viscid residue, soluble in water. — 5. Its solution in hydrochloric acid when boiled, gives off chloride of ethyl with a small quantity of alcohol, the citric ether being decomposed. — 6. Its solution in water gradually turns sour, most quickly when heated. — 7. Ammoniacal gas has no action upon citric ether; but aqueous ammonia gradually yields citrate of ammonia and alcohol; a similar action is exerted by aqueous potash or soda at the boiling heat (as first observed by Thénard). — *Baryta*, or *lime-water*, does not produce turbidity in the ether, or in its aqueous solution. — *Potassium* introduced into the ether, eliminates but a small quantity of gas, perhaps arising from a trace of water. — *Chlorine-gas* does not decompose the ether, even at 110°, or in sunshine. — *Bromine* dissolved in it, evaporates when heated, but nevertheless leaves an acid residue. (Malaguti.) — [Alcoholic ammonia converts citric ether into citramide.]

*Combinations.* The ether is sparingly soluble in *water*. It dissolves in cold *oil of vitriol*, and in strong *hydrochloric acid*, and is separated from both solutions by water, in its original state; whereas from its solution in cold *nitric acid* it is not separated by water.

It dissolves *bromine* and *iodine;* the latter solution is neither decolorised nor rendered acid by heat; neither is it altered by water, alcohol, or ether, but nitric acid throws down iodine from it; the combination appears therefore to be more intimate than that formed by bromine.

Citric ether dissolves in *vinic ether;* and in *alcohol* even when dilute. (Malaguti.)

## ¶. Citramide. $C^{12}N^3H^{11}O^8$.

Obtained by the action of alcoholic ammonia on citric ether. (Demondesir, *Compt. rend.* 33, 227.)

$$3C^4H^5O,C^{12}H^5O^{11} + 3NH^3 = 3C^4H^6O^2 + C^{12}N^3H^{11}O^8.$$

May be regarded as tribasic citrate of ammonia *minus* 6 At. water.

$$C^{12}H^5(NH^4)^3O^{14} - 6HO = C^{12}N^3H^{11}O^8.$$

## ¶. Citranilic Acid.
$$C^{24}NH^{11}O^{10} = C^{12}(C^{12}H^5O^6)AdH^4,O^4.$$

L. Pebal. *Ann. Pharm.* 82, 92.

*Citromonanilsäure, Acide phényl-citramique.*

Obtained by the action of heat on monobasic citrate of aniline:

$$C^{12}NH^7,C^{12}H^8O^{14} - 4HO = C^{24}NH^{11}O^{10}.$$

When the citrate of aniline is kept in the fused state, between 140° and 150°, as long as water is given off, the residue solidifies, for the most

part even while hot, and partly on cooling, in a crystalline mass, which dissolves readily in water, and if care has been taken to avoid using an excess of aniline, is deposited by spontaneous evaporation in crystalline spherules, or in mammellated crusts composed of small prisms. The solution is then treated with animal charcoal, and the product purified by recrystallisation. The crystals dissolve readily in alcohol, and their solutions redden litmus-paper.

| *Dried over oil of vitriol.* | | | | Pebal. |
|---|---|---|---|---|
| 24 C | 144 | .... | 57·83 | ........ 57·71 |
| N | 14 | .... | 5·62 | |
| 11 H | 11 | .... | 4·42 | ........ 4·58 |
| 10 O | 80 | .... | 32·13 | |
| $C^{24}NH^{11}O^{10}$ | 249 | .... | 100·00 | |

The acid treated with pentachloride of phosphorus, gives off hydrochloric acid, and gradually forms a liquid, which appears to contain *chloride of aconitanil*, $C^{24}NH^{8}O^{6},Cl$, inasmuch as when treated with water, it is resolved into hydrochloric and aconitanilic acids (p. 408.)

*Silver-salts.* — *a. Neutral.* — Obtained by mixing an alcoholic solution of the acid neutralized with ammonia, with aqueous nitrate of silver; a white precipitate is then produced, and the filtrate deposits neutral citranilate of silver in crystalline spherules.

| *Dried over oil of vitriol.* | | | | Pebal. |
|---|---|---|---|---|
| 24 C | 144 | .... | 40·44 | ........ 39·97 |
| N | 14 | .... | 3·93 | |
| 10 H | 10 | .... | 2·81 | ........ 2·86 |
| Ag | 108 | .... | 30·35 | ........ 30·93 |
| 10 O | 80 | .... | 22·47 | |
| $C^{24}NH^{10}AgO^{10}$ | 356 | .... | 100·00 | |

The deficiency of carbon and excess of silver probably arose from a slight admixture of the following salt.

*b. Basic.* — Formed by saturating an aqueous solution of the acid with ammonia, and precipitating with nitrate of silver. White curdy precipitate, which may be purified by washing with water and pressure between paper.

| *Dried over oil of vitriol.* | | | | Pebal. |
|---|---|---|---|---|
| 24 C | 144 | .... | 29·93 | ........ 30·17 |
| N | 14 | .... | 2·91 | |
| 11 H | 11 | .... | 2·29 | ........ 2·41 |
| 2 Ag | 216 | .... | 44·92 | ........ 44·65 |
| 12 O | 96 | .... | 19·95 | |
| $AgO,C^{24}NH^{10}AgO^{10} + Aq$ | 481 | .... | 100·00 | |

Pebal regards this salt as belonging to a bibasic citranilic acid, $C^{24}NH^{13}O^{12}$ or $2HO,C^{24}NH^{11}O^{10}$, which however he has not been able to isolate.

*Aniline-salt.* — Obtained by saturating citranilic acid with aniline. Spherical groups of crystals very soluble in alcohol. When dried over oil of vitriol, they give off only a small quantity of hygroscopic water. (Pebal.)

| *Crystals dried over oil of vitriol.* | | | Pebal. |
|---|---|---|---|
| 36 C | 216 | 63·16 | 63·05 |
| 2 N | 28 | 8·19 | |
| 18 H | 18 | 5·26 | 5·34 |
| 10 O | 80 | 23·39 | |
| $C^{12}NH^7,C^{24}NH^{11}O^{10}$ | 342 | 100·00 | |

## ¶. Citrobianil.

$$C^{36}N^2H^{16}O^8 = C^{24}(C^{12}H^5O^6)NAdH^9,O^2.$$

PEBAL. *Ann. Pharm.* 82, 87.

*Phényl-citrimide.*

Obtained, together with citranilide and citranilic acid, by heating citric acid with a slight excess of aniline to a temperature between 140° and 150°, as long as bubbles of vapour of water and aniline are given off. The mixture forms on cooling, a brown-red glass, which, when boiled with water, yields a solution of citranilic acid, and a pale yellow residue, soluble in alcohol. The alcoholic solution, decolorised with animal charcoal, yields thin prismatic crystals of citranilide, and hexagonal tables of citrobianil. — The latter substance may be obtained separately by mixing citric acid and aniline in the proportion required to form a bibasic salt, and heating the mixture to 150° as long as water is given off. — It is also obtained by heating citranilic acid with aniline to about 150°.

$$C^{24}NH^{11}O^{10} + C^{12}NH^7 = C^{36}N^2H^{16}O^8 + 2HO.$$

The crystals are purified by treatment with animal charcoal and recrystallisation.

Transparent, colourless, six-sided laminæ or tables, which are permanent in the air, and do not diminish in weight when left over oil of vitriol. — [For the crystalline form *vid.* Schabus, *Bestimmung der Krystallgestalten in chem. Laborat. erzeugt. Produkte;* Wien, 1855. — The alcoholic solution is neutral to test-paper.

| *Dried over oil of vitriol.* | | | Pebal. |
|---|---|---|---|
| 36 C | 216 | 66·66 | 66·51 |
| 2 N | 28 | 8·64 | |
| 16 H | 16 | 4·94 | 5·04 |
| 8 O | 64 | 19·76 | |
| $C^{36}N^2H^{16}O^8$ | 324 | 100·00 | |

$= 2C^{12}NH^7,C^{12}H^8O^{14} - 6HO$ = bibasic citrate of aniline *minus* 6 At. water.

The alcoholic solution of the product obtained by heating the mixture of citric acid and aniline (p. 405), yielded, besides the crystals of citranilide and the hexagonal

tables of citrobianil, also four-sided obliquely truncated needles, which effloresced over oil of vitriol, and after being dried in the air lost 1·08 p. c. of their weight when heated to 100°. These crystals dried at 100°, were found to contain 66·71 p. c. C, and 5·00 H, which agrees with the formula of citrobianil; but the quantity obtained was too small for exact identification.

Citrobianil heated for some time to 160° in a sealed tube with dilute hydrochloric acid, yields a watery liquid, containing hydrochlorate of aniline and citranilic acid, and a soft mass containing citrobianilic acid. — By ammonia at the boiling heat it is converted into citrobianilic acid.

Citrobianil dissolves very sparingly in *water*, readily in *alcohol*. (Pebal.)

## ¶. Citrobianilic Acid.

$$C^{36}N^2H^{18}O^{10} = C^{24}(C^{12}H^5O^6)Ad^2H^9,O^4.$$

PEBAL. *Ann. Pharm.* 82, 89; 98, 91.

*Citrobianilsäure, Acide phényl-citrobiamique.*

Obtained in the form of an ammonia-salt by boiling citrobianil with ammonia:

$$C^{36}N^2H^{16}O^8 + 2HO = C^{36}N^2H^{18}O^{10};$$

or by heating citranilide with ammonia to 165° in a sealed tube, aniline being formed at the same time:

$$C^{48}N^3H^{23}O^8 + 2HO = C^{36}N^2H^{18}O^{10} + C^{12}NH^7.$$

The solution of the ammonia-salt treated with hydrochloric acid, yields citrobianilic acid in the form of a curdy precipitate which dissolves in alcohol, and crystallises therefrom in soft concentrically grouped needles having a silky lustre.

| *Dried over oil of vitriol.* | | | Pebal. |
|---|---|---|---|
| 36 C | 216 | 63·16 | 63·07 |
| 2 N | 28 | 8·19 | |
| 18 H | 18 | 5·26 | 5·41 |
| 10 O | 80 | 23·39 | |
| $C^{36}N^2H^{18}O^{10}$ | 342 | 100·00 | |

$$= 2C^{12}NH^7,C^{12}H^8O^{14} - 4HO.$$

The acid melts at about 153°, giving off water and being converted into citrobianil. — Heated in a sealed tube, it yields aniline, and probably also citranilic acid:

$$C^{36}N^2H^{18}O^{10} = C^{12}NH^7 + C^{24}NH^{11}O^{10}.$$

Heated with aniline, it yields citranilide and water:

*Combinations.* The acid dissolves sparingly in *water*.

It is monobasic, the formula of its *salts* being $C^{36}N^2H^{17}MO^{10}$.

*Baryta-salt*, $C^{36}N^2H^{17}BaO^{10}$. — Chloride of barium, added to an aqueous solution of the ammonia-salt, throws down a white, amorphous precipitate, which, after being washed, pressed between paper and dried at 80°, bakes together at 100°, and absorbs moisture from the air. The salt dried at 80° contains 18·48 p. c. baryta.

*Silver-salt.* — A neutral solution of the acid in dilute ammonia forms with nitrate of silver, a white precipitate, which, when washed with water, pressed between bibulous paper, and dried over oil of vitriol, exhibits the following composition:

| | | | Pebal. |
|---|---|---|---|
| 36 C | 216 | 48·10 | 47·81 |
| 2 N | 28 | 6·23 | |
| 17 H | 17 | 3·78 | 3·87 |
| Ag | 108 | 24·07 | 24·01 |
| 10 O | 80 | 17·82 | |
| $C^{36}N^2H^{17}AgO^{10}$ | 449 | 100·00 | |

*Aniline-salt.* — The solution obtained by digesting the acid with warm aqueous aniline, yields the salt by evaporation, in colourless, transparent laminæ, which lose but little of their weight when placed over oil of vitriol.

| | | | Pebal. |
|---|---|---|---|
| 48 C | 288 | 66·21 | 66·18 |
| 3 N | 42 | 9·65 | |
| 25 H | 25 | 5·75 | 5·89 |
| 10 O | 80 | 18·39 | |
| $C^{12}NH^7,C^{36}N^2H^{18}O^{10}$ | 435 | 100·00 | |

The acid dissolves readily in *alcohol*. (Pebal.)

## ¶. Citranilide.

$$C^{48}N^3H^{23}O^8 = C^{36}(C^{12}H^5O^6)NAd^2H^{14},O^2.$$

PEBAL. *Ann. Pharm.* 82, 86.

*Citronanilid, Phényl-citramide.*

*Preparation* (p. 465). — Dissolves very sparingly, or not at all in water, and not very easily in boiling alcohol, from which, however, it is deposited by spontaneous evaporation, in colourless, flat, perpendicularly truncated prisms, longitudinally striated, having a mother-of pearl lustre, and generally arranged in concentric groups. The crystals do not lose weight when placed over oil of vitriol. Their solution is neutral to vegetable colours. They are not perceptibly altered by boiling with potash-ley of sp. gr. 1·27, or with strong ammonia, and may therefore be freed in this manner from the adhering six-sided tables of citrobianil which are dissolved by the alkali.

| | | | | Pebal (*mean*). |
|---|---|---|---|---|
| | *Dried over oil of vitriol.* | | | |
| 48 C | 288 | .... | 69·06 | 69·08 |
| 3 N | 42 | .... | 10·07 | 10·43 |
| 23 H | 23 | .... | 5·52 | 5·64 |
| 8 O | 64 | .... | 15·35 | |
| $C^{48}N^{3}H^{23}O^{8}$ | 417 | .... | 100·00 | |

$= 3C^{12}NH^{7}, C^{12}H^{8}O^{14} - 6HO$ = tribasic citrate of aniline *minus* 6 At. water. (Pebal.)

¶. *Oxychlorine-nucleus* $C^{12}H^{8}Cl^{2}O^{4}$.

## Oxychlorocitric Acid.

$$C^{12}H^{8}Cl^{2}O^{12} = C^{12}H^{8}Cl^{2}O^{4},O^{8}.$$

PEBAL. *Ann. Pharm.* 98, 71.

*Oxychlorure de citryle.*

*Preparation.* By the action of pentachloride of phosphorus on dry citric acid (p. 440). The mass becomes heated and liquefies at first, but on cooling solidifies in a magma of crystals consisting of oxychlorocitric acid mixed with oxychloride of phosphorus. To separate the latter substance, the mass is mixed with 3 or 4 times its weight of sulphide of carbon, the lumps being broken up with a glass rod; the whole then thrown on a filter and washed with sulphide of carbon; and the colourless crystals which remain, freed from sulphide of carbon by pressure between paper and drying in vacuo, or by passing a stream of dry air over them.

Colourless silky needles.

| | | | | Pebal (*mean*). |
|---|---|---|---|---|
| 12 C | 72·0 | .... | 29·17 | 29·25 |
| 8 H | 8·0 | .... | 3·24 | 2·39 |
| 2 Cl | 70·8 | .... | 28·69 | 28·55 |
| 12 O | 96·0 | .... | 38·90 | |
| $C^{12}H^{8}Cl^{2}O^{8}$ | 246·8 | .... | 100·00 | |

The acid heated to 100° in a current of air gives off hydrochloric acid, melts, turns brown, and yields aconitic acid in a semicrystalline form :

$$C^{12}H^{8}Cl^{2}O^{12} = 2HCl + C^{12}H^{6}O^{12}.$$

The crystals in contact with water or moist air, become heated and are converted into citric acid.

$$C^{12}H^{8}Cl^{2}O^{12} + 2HO = C^{12}H^{8}O^{14} + 2HCl.$$

Dry ammoniacal gas acts violently on the acid, forming a black vesicular mass. — In contact with anhydrous aniline, the acid becomes strongly heated, and yields aconitobianil (p. 409).

$$C^{12}H^{8}Cl^{2}O^{12} + 2C^{12}NH^{7} = C^{36}N^{2}H^{14}O^{6} + 2HCl + 6HO. \text{ ¶.}$$

*Oxyamidogen-nucleus* $C^{12}AdH^{9}O^{4}$.

## Lactamic Acid.

$$C^{12}NH^{11}O^{8} = C^{12}AdH^{9}O^{4},O^{4}.$$

PELOUZE. *N. Ann. Chim. Phys.* 13, 260, also *Ann. Pharm.* 53, 115.
LAURENT. *Compt. rend.* 20, 512. — *Compt. chim.* 1845, 151.

The lactamide which Pelouze discovered in 1845, was found by Laurent to be lactamate of ammonia.

*Lactamate of Ammonia.* — *Pelouze's Lactamide.* — 1. Lactide absorbs ammoniacal gas with rise of temperature, gradually assuming the liquid form, and being finally converted into lactamide $NH^{3}, C^{12}H^{8}O^{8}$, which crystallises from alcohol in right rectangular prisms. (Pelouze.) With aqueous alkalis, but only when heated, and very slowly even then, it gives off ammonia, and leaves a salt of lactic acid. It dissolves in water without decomposition; but when the solution is heated in close vessels, at temperatures above 100°, it is converted into lactate of ammonia. It does not combine, either with acids or with bases. It dissolves abundantly in alcohol, and crystallises when the solution is cooled or evaporated. (Pelouze.)

2. Lactic anhydride absorbs 2 At. dry ammoniacal gas. In this compound $= 2NH^{3},C^{12}H^{10}O^{10}$ (probably $2NH^{3},C^{12}H^{8}O^{8} + 2HO$), the ammonia can be detected by ordinary reagents. (Pelouze.) — Lactic anhydride dissolved in absolute alcohol and saturated with ammonia, yields, by evaporation and cooling, tabular crystals, very easily soluble in water and alcohol, agreeing in character with Pelouze's lactamide, and containing:

| | *Tables* (2). | | Laurent. |
|---|---|---|---|
| 12 C | 72 | 40·45 | 40·0 |
| 2 N | 28 | 15·73 | |
| 14 H | 14 | 7·87 | 7·8 |
| 8 O | 64 | 35·95 | |
| $C^{12}AdH^{8}(NH^{4})O^{8}$ | 178 | 100·00 | |

The above-mentioned alcoholic solution of the anhydride saturated with ammonia, if freed by boiling from excess of ammonia, gives with excess of bichloride of platinum, a precipitate of chloroplatinate of ammonium; but the liquid filtered therefrom yields, after being boiled for an hour, a fresh precipitate, a proof that only part of the ammonia is contained in the compound in its ordinary state. The compound which

crystallises in tables is therefore lactamate of ammonia $= NH^3C^{12}AdH^9O^8 = C^{12}AdH^8(NH^4)O^8$; and lactamic acid is $C^{12}AdH^9O^8 = C^{12}AdH^9O^4,O^4$. (Laurent.) [It still remains to explain the contradictory statement, that the crystals obtained by Pelouze's method (1) give off ammonia only when boiled with aqueous alkalis for a considerable time, whereas the alcoholic solution of the anhydride saturated with ammonia (2), when freed from excess of ammonia by boiling, and then boiled with chloride of platinum, immediately deposits a portion of the ammonia in the form of chloroplatinate of ammonium.]

*Primary nucleus* $C^{12}H^{18}$.

*Oxygen-nucleus* $C^{12}H^{12}O^6$.

## Lactic Acid.

$C^{12}H^{12}O^{12} = C^{12}H^{12}O^6,O^6$.

SCHEELE. *Opusc.* 2, 101.
BERZELIUS. *Schw.* 10, 105. — *Berz. Jahresber.* 2, 72; 7, 2, 299; *Pogg.* 19, 26.
BRACONNOT. *Ann. Chim.* 86, 84.
A. VOGEL. *Schw.* 20, 425.
JULES GAY-LUSSAC & PELOUZE. *Ann. Chim. Phys.* 52, 410; also *Pogg.* 29, 108; also *Ann. Pharm.* 7, 40.
CAP & HENRY. *J. Pharm.* 25, 138; also *Ann. Pharm.* 30, 106.
CORRIOL. *J. scienc. phys.* 3, 241. — *J. Pharm.* 19, 373.
BOUTRON & FREMY. *N. Ann. Chim. Phys.* 2, 257; also *J. Pharm.* 27, 324; also *Ann. Pharm.* 39, 181; also *J. pr. Chem.* 24, 364.
PELOUZE. *N. Ann. Chim. Phys.* 13, 256; also *N. J. Pharm.* 7, 1; also *Ann. Pharm.* 53, 112; also *J. pr. Chem.* 35, 128.
ENGELHARDT & MADDRELL. *Ann. Pharm.* 63, 83; 70, 241.
ENGELHARDT. *Ann. Pharm.* 65, 359.
A. STRECKER. *Ann. Pharm.* 81, 247; 91, 352.

*Milchsäure, Acide lactique, Acide nancéique, Acide zumique.* — Discovered by Scheele in sour milk; regarded by Bouillon Lagrange (*A. Gehl.* 4, 560) and by Fourcroy & Vauquelin (*N. Gehl,* 2, 622), as a compound of acetic acid with animal matter; again recognised as a peculiar acid by Berzelius, who found it in most animal substances; discovered a second time, as *nanceic acid,* by Braconnot, who regarded the existence of lactic acid as disproved. More recently, the separate existence of the acid of sour milk was incontestably established by Gay-Lussac, Pelouze, Boutron, Fremy & Engelhardt, whereas the acid of flesh is still admitted by Liebig & others to exhibit differences. The *caseic acid* of Proust (*Ann. Chim. Phys.* 10, 33; also *N. Tr.* 4, 1, 212), produced in the putrefaction of cheese or gluten under water, in which Braconnot (*Ann. Chim. Phys.* 35, 159; also *N. Tr.* 18, 270) also found leucin, an animal substance soluble in water and alcohol and precipitable by tannin, a partially resinised oil having a burning taste, but in other respects resembling butyric acid, also acetic acid, and small quantities of chloride of potassium and acetate of potash — may consist chiefly of lactic acid.

*Sources.* 1. In vegetable substances which have turned sour (p. 474.) —2. In many parts of the animal body, sometimes free, sometimes combined with alkalis, as in flesh, blood, milk, urine, &c. (Berzelius); also in the yolk of egg (Gobley, *N. J. Pharm.* 9, 165), and in the gastric juice. (Bernard, Barreswil, Lassaigne.) Respecting the occurrence of this acid in the animal body, there is however a two-fold doubt,—inasmuch as, on the one hand, the occurrence of lactic or a similar acid in the blood has been disproved by Enderlin (*Ann. Pharm.* 46, 164); and its occurrence in the urine (from which Lehmann, *J. pr. Chem.* 25, 15, states that he obtained lactate of zinc, which however may have been the compound of cratinine with chloride of zinc), has been disproved by Liebig (*Ann. Pharm.* 62, 337) and by Heintz (*Pogg.* 62, 602), —and its existence in the gastric juice has been shown to be improbable by Blondlot (*J. Chim. méd.* 20, 386), and by Enderlin (*Ann Pharm.* 46, 122);—while on the other hand the acid of flesh is perhaps only isomeric with lactic acid.

*Formation.* 1. In the oxidation of alanine (ix, 434) by nitrous acid. —When the nitrous vapours evolved from starch and nitric acid are passed, first through a cold vessel which stops the admixed nitric acid, and then into aqueous alanine, nitrogen gas is evolved in large quantity till the alanine is completely decomposed, and likewise a small quantity of nitric oxide (proceeding from the decomposition of the nitrous acid by the water), and a very acid liquid is formed, which, when gently evaporated to a syrupy consistence, and then shaken up with ether, gives up to the ether a quantity of lactic acid possessing all its characteristic properties :

$$C^6NH^7O^4 + NO^3 = C^6H^6O^6 + HO + N^2.$$

[or doubled; $2C^6NH^7O^4 + 2NO^3 = C^{12}H^{12}O^{12} + 2HO + N^4$.] (Strecker.)

This is the most striking example known of the formation of an organic compound of higher from one of lower grade. (Compare vii, 42.)

2. In the *lactic acid fermentation* of glucose, common sugar, milk-sugar and dextrin. This fermentation precedes the butyric acid fermentation. As all these substances contain $C^{24}$, $H^{24}$ and $O^{24}$, in some cases with a few atoms of HO more or less, their conversion into lactic acid is explained by the splitting up of an atom so constituted into two, and a new juxtaposition of the simple atoms. Thus, $C^{24}H^{20}O^{20}$ (milk-sugar) + 4HO = $2C^{12}H^{12}O^{12}$. — Compare the observations of Pelouze & Gelis on the butyric acid fermentation (x, 77).—The lactic acid fermentation requires, in addition to the above-mentioned sweet substances, a peculiar ferment, water, and a temperature between 20° and 40°, but no air, provided the ferment is previously completely developed. The *ferments* which induce lactic acid fermentation, are generally protein-substances which have undergone some alteration by the action of air and water, and, according to the degree of that alteration, are capable of converting the sugar into mannite, gum, alcohol, or lactic acid. (Boutron & Fremy.)

1. *Casein.* [As milk does not turn sour till after the lapse of some days, the change appears to be preceded by the conversion of the casein dissolved in it into the ferment by the action of oxygen].—When milk turns sour in warm air, only a part of the milk-sugar is converted into lactic acid, unless this acid be repeatedly neutralised with lime, inasmuch as, by com-

bining with the casein, it interferes with the fermenting power of that substance. Sour cheese washed with water till it no longer reddens litmus, and dissolved in dilute carbonate of soda, forms with milk-sugar an acid liquid, the quantity of lactic acid in which continually increases by repeated neutralisation with carbonate of soda and addition of milk-sugar; nevertheless the casein (perhaps by conversion into another kind of ferment) ultimately loses its power of converting further quantities of milk-sugar into lactic acid. The milk which has turned sour likewise passes into a state of putrefaction, unless the power of forming lactic acid be restored by removal of the acid already formed. (Boutron & Fremy.)

2. *Altered Gluten and substances of like nature. Diastase* exposed for two or three days to moist air, converts sugar and starch, in presence of water, into lactic acid, without formation of gas; the starch is probably first converted into dextrin. — Slightly moistened *barley-malt*, which has been exposed to the air for two or three days, forms with water at temperatures between 20° and 30°, lactic acid (but no mannite) and ultimately, in consequence of a further alteration of the diastase, renders the liquid turbid and deposits wine-ferment, which then sets up vinous fermentation. If the malt has been heated to 100° with the water for a length of time different from that above stated, little or no lactic acid is produced. (Boutron & Fremy.) — *Wheat-flour* made up with water to a stiff paste, or moist gluten left in a warm place for two days, changes to a lactic acid ferment having a disagreeable odour of sour milk, and after a longer time to a vinous ferment, the odour of which is less unpleasant. (Fownes, *Phil. Mag. J.* 21, 355.) — The *coagulum* from *almond-milk* which has turned sour converts a solution of common sugar completely into lactic acid, acetic acid and gum. (Boutron & Fremy.)

3. *Animal Membranes.* — The well washed *coating of the stomach* of the calf or dog, after being kept for a short time under water, acquires the power of converting sugar into lactic acid; and well dried animal bladder, though it remains a long time inactive in dry air, nevertheless acquires by exposure to moist air, the power of converting sugar into lactic acid or a similar acid, the lime-salt of which is however insoluble in alcohol. (Boutron & Fremy.) — When the filtered liquid obtained by stirring up comminuted calf's liver with water is mixed with carbonate of lime and set aside at a temperature between 25° and 35°, it enters into rapid fermentation, but without emitting any unpleasant odour, and the sugar contained in the liver is converted into lactic acid identical with that which is obtained from milk. (Dessaignes, *N. J. Pharm.* 25, 29.)

The following substances, from containing these ferments and sugar, likewise pass into the state of lactic acid fermentation. The *sour water* which runs off in the preparation of starch (Corriol); *beans, peas, rice* or *sour dough*, and *juice of mangold-wurzel* set aside in contact with water (Braconnot); *decoction of oats* or *milk of almonds* (A. Vogel); *Sauerkraut*, without any acetic acid (Liebig, *Ann. Pharm.* 23, 113); pickled *white carrots* (Wittstein, *Repert.* 65, 370); fermenting *pickled cucumber*, till butyric acid begins to form (Marchand, *J. pr. Chem.* 32, 506); *Nux vomica* set aside with water (Corriol, *J. Pharm.* 11, 402; 19, 155 and 373, and *J. scienc. Phys.* 3, 241). The *sour tan-liquor* obtained by exhausting with water the bark which has been used for tanning, is also rich in lactic acid. (Braconnot, *Ann. Chim. Phys.* 50, 376; also *Schw.* 66, 320; also *Ann. Pharm.* 5, 275.) The juice of the *edible boletus* fermented with carbonate of lime, likewise yields a considerable quantity of lactate of lime. (Dessaignes.)

During the lactic acid fermentation, there is often formed, in addition to lactic acid, a gummy substance, and a peculiar acid whose lime-salt dissolves more abundantly in absolute alcohol than lactate of lime, and in the crystallised state contains $CaO,C^{20}H^{14}O^{4} + 12$ Aq. (Engelhardt & Maddrell.)

The subsequent conversion of the lactic acid formed in the earlier stage of the fermentation into butyric acid, appears to result from the action of the same ferment. Perfectly pure lactate of lime dissolved in water, and kept at a temperature of 30° for six weeks, does not yield any butyric acid; but the lime-salt which has been but imperfectly freed from cheese by two crystallisations, and is otherwise free from fat, or pure lactate of lime prepared from the pure acid and carbonate of lime, and mixed with cheese, does yield butyric acid when similarly treated. (Engelhardt & Maddrell.)

Grape-sugar mixed with cheese is converted into lactic acid more quickly than common sugar. Starch (compare, however, Gobley, p. 476), and mannite mixed with water and cheese do not enter into the lactic acid fermentation. (H. v. Blücher, *Pogg.* 63, 424.)

The juice of mountain-ash berries neutralised with carbonate of lime, and mixed with yeast, enters into fermentation at ordinary temperatures, yielding principally lactic acid with a very small quantity of succinic acid. (W. Baer, *Arch. Pharm.* [2], 69, 147.) The acid residue of cider contains a considerable quantity of lactic acid, probably resulting from the fermentation of lactate of lime contained in the juice of the apples. (Winckler *Jahrb. pr. Pharm.* 22, 300.)

The presence of *nicotine* interferes with the lactic acid fermentation. (E. Robin, *Compt. rend.* 32, 773.)

*Preparation.* I. *From various kinds of Sugar.* — 1. An aqueous solution of 100 pts. of grape-sugar (cane or milk-sugar), exhibiting the density of 8° to 10° Bm. is mixed with 8 or 10 pts. of fresh sour cheese, as purchased in the market, — or 100 pts. of sugar are dissolved in 100 to 150 pts. of milk, and such a quantity of water that the liquid exhibits a density of 10° Bm., and either of these mixtures is placed, together with 50 pts. of chalk, in an open vessel, and exposed to the sun for several weeks with frequent agitation, till the resulting lactate of lime begins to change into butyrate. (Pelouze and Gelis.) As lactate of lime is much less soluble than butyrate, the conversion of the former into the latter may be recognised, when strong solutions of sugar are used, by the diminution of the crystalline mass produced at first. If the process be too soon interrupted, a large quantity of sugar remains unaltered.

2. Six pounds of cane-sugar and half an ounce of tartaric acid (which serves to convert the cane-sugar into glucose) are dissolved in 26 pounds of boiling water; 3 pounds of levigated chalk added after two days, together with 4 oz. of stinking hand-cheese, suspended in eight pounds of sour milk (decaying cheese favours the production of lactic acid and retards its conversion into butyric acid); the mixture set aside at a temperature between 30° and 35°, and well stirred every day, till, in the course of six or eight days, it is converted into a stiff paste of lactate of lime; this paste boiled for an hour with half an ounce of quick lime and 20 pounds of water; the solution strained through a cloth filter and evaporated to a syrup; the crystalline mass which forms in four days, pressed, first by itself, then three or four times, after having been each time stirred up, with $\frac{1}{10}$ pt. of cold water; and the lactate of lime thus

purified is dissolved in twice its weight of boiling water. To the solution of every 32 pts. of the lime-salt there is then added a mixture of 7 pts. oil of vitriol and 7 pts. water; the lactic acid, while still hot, strained through linen to separate it from sulphate of lime; the filtrate obtained from 7 pts. of oil of vitriol boiled with $1\frac{3}{8}$ pts. carbonate of zinc for a quarter of an hour (by longer boiling a very sparingly soluble basic salt is formed); the liquid filtered boiling hot; the colourless crystalline grains of lactate of zinc which separate on cooling, freed from sulphuric acid by washing with cold water; and additional quantities of crystalline grains obtained by evaporating the mother-liquor, almost to the end. Lastly, 1 pt. of the zinc-salt is dissolved in $7\frac{1}{2}$ pts. of boiling water; sulphuretted hydrogen passed through the solution as long as sulphide of zinc is precipitated; and the filtrate boiled and evaporated on the water-bath to a syrup, whereupon 8 pts. of the zinc-salt yield 5 pts. of syrupy lactic acid. (Bensch, *Ann. Pharm.* 61, 174.) — By this process, 100 pts. of cane-sugar yield 117 pts. of lactate of lime, which, if the sugar was white, is colourless, and does not require to be purified by pressure. If the carbonate of zinc contains lime and magnesia, these bases pass over to the lactic acid, which, after being evaporated to a syrup, must be dissolved in ether, and separated from the lactates of lime and magnesia by filtration and evaporation. The lime-salt may however, without first preparing the zinc-salt from it, be freed by repeated crystallisation from a nitrogenous substance which obstinately adheres to it; its solution in the smallest possible quantity of water, mixed with a quantity of pure sulphuric acid not quite sufficient to decompose it; the mixture heated with alcohol till the sulphate of lime is completely separated; the filtrate evaporated to a syrup; the syrup dissolved in ether; and the ethereal solution filtered and evaporated. (Engelhardt & Maddrell.)

3. Into a stone-ware jar holding 3 litres, are introduced 250 grammes of milk-sugar, 200 grm. of powdered chalk, 1 litre of skimmed milk and sufficient water to fill the jar, and the mixture is then exposed to a temperature between 25° and 30°, frequently stirred, and the water replaced as it evaporates, till the evolution of carbonic acid ceases, a sour and cheese-like odour becomes perceptible, and the chalk-powder has become granular,—a change which takes place in about 12 days. The liquid is then boiled for a quarter of an hour, and separated from the cheese by straining through flannel; the residue washed with boiling water; the whole of the liquid diluted with water, filtered through paper, and evaporated at a gentle heat; the lactate of lime which separates after 24 hours, as well as that which is obtained by further evaporation and setting the mother-liquor aside, strongly pressed between canvas, and the cake broken up and dried in the hot air chamber. The product amounts to 340 grammes.

In a similar manner, lactate of lime may be obtained: From 250 grammes of dextrin, 200 grm. of chalk, 2 litres of milk and half a litre of water; from 250 grm. cane-sugar, 200 grm. chalk, 2 litres of milk and half a litre of water left for 8 days at a temperature between 25° and 30° (if it be left for a longer time, a considerable quantity of the lactic acid is converted into butyric acid); and at lower temperatures (15° to 20°) a viscous fermentation goes on, whereas between 25° and 30°, provided there is no deficiency of ferment, nothing but lactic acid fermentation takes place, and in 8 days, 280 pts. of lactate of lime are obtained); — from pulverised wheat-starch, and the other materials above-mentioned added in the same proportion (in 24 hours, brisk but not viscous fermenta-

tion; the starch, which during the first days remains in a thick layer at the bottom of the vessel, gradually dissolves); — from gum arabic, with the same additions in the same proportions as with cane-sugar, but without water (the fermentation, which is not viscous, begins in 24 hours, but in 10 days produces only a small quantity of lactate of lime). — Beer-yeast also, instead of milk, produces lactic acid with milk-sugar, cane-sugar, dextrin, starch, or gum. (Gobley, *N. J. Pharm.* 6, 54.)

4. A mixture of 25 pts. of milk-sugar, 20 pts. of chalk-dust, 100 pts. of skimmed milk, and 200 pts. of water, is set aside for 44 days at a temperature of 24°, till all the chalk is dissolved; the acid liquid then heated (but not to the boiling point); the curd strained by pressure; the turbid liquid clarified by decantation, straining through grey paper, and boiling with white of egg; the solution of lactate of lime evaporated to the crystallising point, and the salt recrystallised several times from hot water. (Wackenroder.)

5. The solution of 300 grammes of milk-sugar in 4 litres of milk, is placed in the open air at a temperature of 25° to 30°, and neutralised with bicarbonate of soda as often as it becomes sour, perhaps every two days; boiled when it no longer turns acid; filtered from the curd; carefully evaporated to a syrup; and the syrup dissolved in moderately warm alcohol of 38° Bm. By treating this filtered alcoholic solution of lactate of soda with sulphuric acid to precipitate the soda, and saturating the filtered lactic acid with chalk, crystallised lactate of lime is obtained, and may be purified by further treatment. (Boutron & Fremy, *J. Pharm.* 27, 341.)

II. *From milk which has turned sour.* — 1. Scheele evaporates sour whey to $\frac{1}{8}$; filters the liquid from the curd; precipitates the phosphoric acid from it with lime; filters; dilutes with 3 pts. water; precipitates the lime by careful addition of oxalic acid; filters; evaporates to the consistence of honey; extracts the lactic acid with alcohol; filters; dilutes with water, and evaporates. Berzelius digests the acid thus obtained with carbonate of lead; filters; precipitates the dissolved lead with sulphuretted hydrogen, filters, and evaporates. — 2. The filtered solution of sour whey evaporated nearly to dryness, in strong alcohol, is mixed with alcoholic tartaric acid, as long as any precipitate of tartrate of potash soda, and lime is formed; the liquid decanted after 24 hours, and evaporated; the residue dissolved in water; the solution digested with carbonate of lead, till lead dissolves in it; the filtrate evaporated, neutralised with carbonate of baryta, again filtered, and diluted with water; the whole of the baryta precipitated by sulphate of zinc; and the filtrate evaporated till lactate of zinc crystallises out. (Berzelius, *Lehrb. Ausg.* 5, v. 241.) For the earlier methods of Berzelius, see *Pogg.* 19, 26. — For Cap and O. Henry's process, *J. Pharm.* 25, 138; also *Ann. Pharm.* 30, 106.

III. *From juice of Mangold-wurzel.* — The syrup, after it has turned sour, is evaporated, (or sour rice-water is evaporated nearly to dryness, the residue exhausted with alcohol, and the solution evaporated to a syrup); the acid diluted with water and saturated with oxide of zinc; the liquid filtered; the lactate of zinc purified by repeated crystallisation; the purified salt dissolved in hot water; the oxide of zinc precipitated; the liquid filtered; the baryta precipitated by the required quantity of sulphuric acid; and the liquid again filtered and evaporated. (Braconnot.)

Any sulphuric acid that may remain mixed with it is precipitated by carbonate of lead, and the lead removed by sulphuretted hydrogen. — 2. The sour juice of mangold-wurzel evaporated to a syrup (or sour whey, or the sour water of the starch-manufacture,) is mixed with hydrate of potash; the magma boiled with alcohol of 36° Bm.; the lactate of lime which remains after the distillation of the alcoholic filtrate dissolved in warm water; the solution filtered and left to crystallise; the crystals purified by repeated crystallisation from alcohol, and finally from water; and the aqueous solution decomposed by the required quantity of oxalic acid. — A similar method is pursued with the rasped nuts of nux vomica, which have been fermented under water, excepting that, in this case, it is not necessary to add any lime-salt, because the fermented liquid, although acid, still contains a sufficient quantity of lime, and that, after the alcohol has been distilled off and the residue dissolved in water, the solution must be filtered to separate fat. (Corriol, *J. scienc. phys.* 3, 241.) 3. Juice of mangold-wurzel is left to stand for two months at a temperature of 25° to 30°, till the fermentation, which is at first violent, and accompanied by the evolution of hydrogen and carbonic acid, is finished; the liquid evaporated to a syrup; this syrup separated from the mannite which crystallises out, and exhausted with alcohol; the alcoholic solution evaporated; the impure lactic acid which remains, dissolved in water; the filtered solution saturated with carbonate of zinc; the crystals of lactate of zinc obtained by evaporating the filtrate, collected and boiled with water and animal charcoal which has been purified by hydrochloric acid; the liquid filtered hot; and the colourless crystals which form on cooling washed with alcohol. From these crystals, the acid is separated by treating them, first with baryta then with sulphuric acid, after which the liquid is evaporated in vacuo, the residue dissolved in ether, and the solution again evaporated after it has deposited a few flocks. If the acid should be still not quite colourless, it must be combined with lime, boiled with animal charcoal, the resulting crystals of the lime-salt recrystallised, first from alcohol then from water, and their solution decomposed by oxalic acid. — In a similar manner; lactic acid may be prepared from sour whey, the acid water of the starch-manufacture, &c. (Jules Gay-Lussac & Pelouze.)

*Separation of Lactic acid from the lime-salt.* — 1. This salt is decomposed by a slight excess of oil of vitriol diluted with a sixfold quantity of water; the liquid mixed with alcohol and filtered from the gypsum; the sulphuric acid precipitated by lactate or acetate of lead; then, after distilling off the alcohol and diluting with water, the lead is precipitated by sulphuretted hydrogen, and the filtrate evaporated over the water-bath. (Berzelius.) — 2. From the dissolved lime-salt, the lime is precipitated by the exactly requisite quantity of oxalic acid. (Braconnot, p. 477; Jules Gay-Lussac and Pelouze, p. 478; J. A. Buchner, *Repert.* 74, 170.) — 3. The lime-salt is converted into a zinc-salt.

*Separation from the zinc-salt.* — 1. By sulphuretted hydrogen. (Bensch.) — 2. By precipitating this zinc with excess of baryta-water, and treating the filtrate with sulphuric acid, any accidental excess of which may be removed by carbonate of lead, the lead being afterwards precipitated by sulphuretted hydrogen. (Jules Gay-Lussac & Pelouze, p. 478.)

The acid may be completely purified by *dissolving* the residue obtained by evaporation in *ether*, filtering from any salts that may be present, and evaporating the ether.

*Properties.* Colourless syrup (Jules Gay-Lussac & Pelouze); nearly colourless (Braconnot).—Brownish (Scheele). Does not solidify at 24°. (Engelhardt & Maddrell.) After complete evaporation in vacuo, it has a specific gravity of 20·5. (Gay-Lussac & Pelouze.) Volatilises without decomposition at 200°, only when a platinum wire is immersed in it. (Pelouze.) Inodorous, has an intolerably biting, pure acid taste. (Gay-Lussac & Pelouze.)

*Syrup dehydrated as completely as possible at* 100°.

| | | |
|---|---|---|
| 12 C | 72 | 40·00 |
| 12 H | 12 | 6·67 |
| 12 O | 96 | 53·33 |
| $C^{12}H^{12}O^{12}$ | 180 | 100·00 |

Gerhardt (*Précis Chim. org.* 1, 596) first raised the formula from $C^6H^6O^6$ to $C^{12}H^{12}O^{12}$; which hypothesis was afterwards adopted more or less by Laurent (*Compt. rend.* 20, 512), Engelhardt & Maddrell, and Strecker (*Ann. Pharm.* 81, 248).—Hypothetical anhydrous lactic acid $\overline{L}$ is according to the old view $C^6H^5O^5$, according to the more recent view $C^{12}H^{10}O^{10}$.—Syrupy lactic acid may be regarded as formic acid + aldehyde = $2(C^2H^2O^4,C^4H^4O^2.)$

*Decompositions.* 1. *Dry distillation.* The acid, when very gradually heated, becomes less viscid; gives off at 130°, slowly and without evolution of gas, colourless water, together with a small quantity of lactic acid, and leaves a pale yellow, solid, easily fusible, extremely bitter residue of lactic anhydride = $C^6H^5O^5$ [$C^{12}H^{10}O^{10}$]. This residue remains unaltered up to 250°, but from 250° to 300°, at which temperature the decomposition is complete, gives off carbonic oxide gas, mixed at first with 4 or 5, and at last with 50 per cent. of its volume of carbonic acid, (altogether a quantity of gas amounting to 33·1 per cent. of the anhydride,) and yields a distillate amounting to 60 per cent. of the anhydride, and consisting of lactide, which crystallises out on cooling and likewise sublimes; of lactone with small quantities of acetone; and an odoriferous oil insoluble in water, whilst a quantity of difficultly combustible charcoal remains, amounting to 6·9 per cent. of the anhydride. (Pelouze.) — The anhydride, which remains undecomposed after heating to 240°, gives off, when kept for some time between 250° and 260°, carbonic oxide mixed with 3 or 4 per cent. of its bulk of carbonic acid gas (without any carburetted hydrogen); yields a yellowish distillate, which deposits crystals of lactide, and contains, in addition to the lactide (amounting to 14·9 per cent. of the anhydride,) nothing but ordinary lactic acid, citraconic acid, (x, 417,) aldehyde (amounting to 12·2 per cent. of the anhydride), but neither acetone nor lactone; and leaves 1 or 2 per cent. of shining, easily combustible charcoal. The aldehyde and the citraconic acid [?] are perhaps merely products of decomposition of the lactide; $C^{12}H^8O^8 = 2C^4H^4O^2 + 4CO$. The ordinary lactic acid is formed from a portion of the anhydride by addition of the water set free by the conversion of the remainder into lactide. If the anhydride be distilled at 300° instead of 260°, less lactic acid and lactide are

obtained, and more aldehyde. (Engelhardt.) Lactic acid, when heated, gives off pungent vapours which excite coughing, and yields a brown empyreumatic oil, together with an acid liquid, the acid of which is neither lactic nor acetic acid, but forms a viscid uncrystallisable salt with oxide of zinc. (Braconnot, *Ann. Chim. Phys.* 50, 375.) — It yields a watery distillate continually becoming more acid, the first portion of which however assumes a syrupy consistence when evaporated in vacuo, and if then gently heated in contact with the air, deposits crystals of lactide; it afterwards yields an oil and then a buttery mass, which solidifies in the neck of the retort, and when exhausted with cold ether, leaves scales and ultimately rhombic laminæ. Lastly, there remains a shining, tumefied charcoal. The acid which remains after partial distillation, likewise contains a certain quantity of lactide, and on boiling this acid with ether and cooling the liquid, the lactide crystallises out. (Corriol.) — By continued heating to between 180° and 200°, the acid is much more quickly converted into the anhydride, and yields a much more copious distillate of the unaltered acid, than between 130° and 140°; and if a platinum wire be immersed in the liquid, the lactic acid may be distilled over quite unaltered and with regular ebullition. (Engelhardt.) — If the lactic acid contains a small quantity of sulphuric acid, it yields only carbonic oxide gas, no carbonic acid. (Pelouze.) If it contains the smallest quantity of impurity, albumen for example, it does not yield any sublimate of lactide. (Gay-Lussac & Pelouze.) — Lactic acid, heated gently in contact with the air, boils gently, emitting a suffocating odour, swells up, blackens, and leaves a spongy charcoal. (Berzelius.)

2. Lactic acid (or ferrous lactate,) mixed with a sixfold quantity of oil of vitriol, and gently heated, froths up briskly, acquires a dark-brown colour; gives off about $\frac{1}{3}$ of its weight of pure carbonic oxide gas; and at a higher temperature, yields about $\frac{1}{3}$ of its weight of a humus-like substance. (Pelouze.)

3. Boiling *nitric acid* converts lactic into oxalic acid. (Jules Gay-Lussac & Pelouze.)

4. Lactic acid and its salts distilled with small quantities of *common salt, peroxide of manganese, sulphuric acid,* and water, yield chiefly aldehyde; with larger quantities, principally chloral. (Städeler, *Ann. Pharm.* 69, 332.)

5. With aqueous *chlorides, of the alkalies* or *chlorous acid,* lactic acid is converted, first into oxalic acid, then with effervescence into carbonic acid. (Cap & Henry.)

6. When treated with *peroxide of barium* or *peroxide of lead,* it is converted chiefly into oxalic acid. (Cap & Henry.)

7. Distilled with *dilute sulphuric acid* and *peroxide of manganese* or *peroxide of lead,* it yields a large quantity of adelhyde, together with carbonic acid. (Liebig.)

*Combinations.* Lactic acid absorbs water from the air, and dissolves in water in all proportions. (Scheele and others.)

*Lactates.* — The acid expels acetic acid from acetate of potash at 100° (as also stated by Scheele), and throws down the sparingly soluble lactate from a cold-saturated solution of acetate of zinc or magnesia. The bibasic (neutral) lactates are $C^{12}H^{10}M^2O^{12}$, and the monobasic (acid) lactates are $C^{12}H^{11}MO^{12}$. The crystalline lactates, which are numerous,

do not effloresce when exposed to the air, but give off water in vacuo, and the whole of it at 100°, the monobasic nickel-salt, however, only at 130°. They sustain a heat of 150° to 170°, without decomposition; the zinc-salt may even be heated to 210°. They dissolve sparingly for the most part in cold water and alcohol, and effloresce rapidly from their solutions, but they are all insoluble in ether. (Engelhardt & Maddrell.)

*Lactate of Ammonia.* — Crystals, which redden litmus, and when heated melt, and give off ammonia. (Braconnot.) The acid mixed with ammonia shows signs of crystallisation, so long as the ammonia is maintained in excess, during the evaporation of the solution; but when further evaporated, it gives off ammonia, and leaves a deliquescent residue, which, when subjected to dry distillation, gives off the greater part of its ammonia, before the acid is decomposed. (Berzelius.) It is only when ammoniacal gas is passed through an ethereal solution of lactic acid, that traces of crystals at first appear; but these, on addition of more ammonia, sink to the bottom of the ether in the form of a syrup. (Engelhardt & Maddrell.) (Dumas, *Ann. Chim. Phys.* 54, 236.) Uncrystallisable, deliquescent. (Pelouze.)

*Lactate of Potash.* — Uncrystallisable, deliquescent; soluble in water and alcohol. (Scheele, Braconnot.) Deliquescent crystalline crust. (Berzelius.) Crystallising with difficulty. (Gay-Lussac & Pelouze.) Syrup which cannot be made to crystallise. (Engelhardt & Maddrell.)

*Lactate of Soda.* — Uncrystallisable, deliquescent. (Scheele, Braconnot.) When the acid somewhat supersaturated with carbonate of soda, is evaporated and exhausted with alcohol, and the alcohol evaporated at 50°, crystals remain covered with a transparent colourless mass, which becomes moist on exposure to the air. (Berzelius.) Uncrystallisable syrup. (Engelhardt & Maddrell.)

*Lactate of Baryta.* — *a. Bibasic.* — By saturating the boiling acid with carbonate of baryta. Transparent, non-deliquescent gum. (Braconnot, Berzelius.) Neutral; dissolves readily in ordinary alcohol; insoluble in cold and very sparingly soluble in boiling absolute alcohol, from which it separates in viscid threads on cooling. (Engelhardt & Maddrell.)

*b. Monobasic.* — By mixing 1 pt. of the acid saturated with carbonate of baryta with 1 pt. more of the acid, crystals are obtained, which may be freed from admixed salt *a* or free acid, by washing with ordinary alcohol. The crystals are very solid, strongly acid, permanent in the air, do not effloresce in a dry vacuum, give off from 2·99 to 3·98 per cent. of water at 100°, with some contraction, and dissolve with tolerable facility in water, but sparingly in cold alcohol of ordinary strength. (Engelhardt & Maddrell.) To this kind probably belong also the crystals described by Braconnot, (*Ann. Chim. Phys.* 50, 375,) which were cauliflower-like, mixed with needles, fusible when heated, and soluble in 21 pts. of cold water.

| *Air-dried crystals.* | | | Engelhardt & Maddrell. |
|---|---|---|---|
| 12 C | 72·0 | 29·08 | 28·57 |
| 11 H | 11·0 | 4·44 | 4·46 |
| BaO | 76·6 | 30·94 | 30·73 |
| 11 O | 88·0 | 35·54 | 36·24 |
| $C^{12}H^{11}BaO^{12}$ | 247·6 | 100·00 | 100·00 |

*Lactate of Strontia.* — *Bibasic.* — By evaporating the aqueous acid saturated with carbonate of strontia, a gummy mass is obtained, which, in 24 hours, solidifies in crystalline grains, soluble in 8 pts. of cold water. (Braconnot.) The grains, which resemble the lime-salt, exhibit a concentrically radiated structure; at the heat of the water-bath, they melt and give off their water of crystallisation. (Blücher, *Pogg.* 63, 429.) They are very much like the lime-salt, and give off 17·70 p. c. (6 At.) water at 100°. (Engelhardt & Maddrell.)

| | *At* 100°. | | Engelhardt & Maddrell. |
|---|---|---|---|
| 12 C | 72 | 27·07 | |
| 10 H | 10 | 3·76 | |
| 2 Sr | 104 | 39·10 | 39·02 |
| 10 O | 80 | 30·07 | |
| $C^{12}H^{10}Sr^{2}O^{12}$ | 266 | 100·00 | |

| | *Air-dried crystals.* | |
|---|---|---|
| 12 C | 72 | 22·5 |
| 16 H | 16 | 5·0 |
| 2 SrO | 104 | 32·5 |
| 16 O | 128 | 40·0 |
| $C^{12}H^{10}Sr^{2}O^{12} + 6Aq$ | 320 | 100·0 |

*Lactate of Lime.* — *a. Bibasic.* — Obtained in the preparation of lactic acid (pp. 475-478), or by saturating the boiling acid with carbonate of lime. — White opaque needles and crystalline grains (Braconnot), composed of delicate, concentrically radiating needles (Corriol, Engelhardt & Maddrell), which under the microscope present the appearance of right rhombic prisms (Wackenroder); they grate between the teeth, are somewhat bitter (Cap & Henry), have but little taste (Corriol). — The air-dried crystals become soft at 80° out of contact with the air; melt at 100° to a colourless syrup, which hardens in the cold; give off the greater part of their water at 135°, then a small additional quantity as the heat rises to 170°, in all 29·17 p. c. (10 At.), while a white frothy mass remains behind. They give off 20·47 per cent. in the air at 80°, afterwards no longer melt at 100°, and give off at this temperature 2·54 p. c. more of water, altogether 22·95 p. c. (or 8 At.); but at 130° the loss amounts in all to 28·0, and at 200° to 29·1 p. c.; from 150° upwards traces of an acid go off. (Wackenroder.) — When heated, they melt into a resinous mass, which becomes crystalline when moistened. (Cap & Henry.) Over oil of vitriol, in air as well as in vacuo, they give off their 29·22 p. c. (10 At.) of water completely. (Engelhardt & Maddrell.) — The crystals melt to a transparent liquid, then froth up, blacken, and take fire. (Braconnot.) — The crystals, when subjected to dry distillation, first give off their water, then solidify, give off carbonic acid and metacetone, and an oil which boils between 160° and 180°, contains 77·42 p. c. C, and 10·84 H. (Favre, *N. Ann. Chim. Phys.* 11, 80; also *J. pr. Chem.* 32, 370). The dry salt remains undecomposed at 180°, then melts at 220°, giving off 1·17 p. c. of empyreumatic vapours. (Engelhardt & Maddrell.) At 250°, it aggregates into an amber-yellow, tumefied gum; then swells up, chars, gives off a brown oil, having an aromatically empyreumatic odour and an acid liquid, which, however, does not contain acetic acid; and finally leaves carbonate of lime, together

with a small quantity of charcoal. (Wackenroder.) The clear, colourless solution of the crystals in cold oil of vitriol, gives off, when heated, carbonic oxide and sulphurous acid gas, (together with an odour of apples, according to Cap & Henry), turns yellow, then black, and afterwards, on addition of water, deposits a large quantity of humus-like matter and gypsum. When the salt is fused for a short time with hydrate of potash, about half of its acid is converted, without charring, into oxalic acid, besides formic and acetic acid. (Wackenroder.)

The crystals are permanent in the air. (Engelhardt & Maddrell.) 1. pt. of the crystals dissolves in 21 pts. of cold water (Braconnot); in 17·4 pts. of water at 24°, and in any quantity of boiling water, in which in fact they melt; the solution of 3 pts. of the salt in 1 pt. of hot water, is a thick syrup, which hardens as it cools. (Wackenroder.) The aqueous solution effloresces in cauliflower-like masses when evaporated. (Engelhardt & Maddrell.) The crystals dissolve in 490 pts. of 85 per cent. alcohol at 20°, but (fusing at the same time according to Engelhardt & Maddrell,) in 1·2 pts. of boiling alcohol of that strength, and, as the liquid cools (nearly all the salt being deposited, according to Corriol,) a magma of slender crystals is produced. (Wackenroder.) The solubility is very slight, even at 50°, and does not increase till the temperature is further raised. The crystals which separate from hot alcohol contain the above-mentioned quantity of water. (Engelhardt & Maddrell.) The alcoholic solution is precipitated by ether, which does not dissolve the salt, in the crystalline form (Pelouze), curdy (Wackenroder.) The dehydrated salt dissolves sparingly in boiling 85 per cent. alcohol (Wackenroder), and the crystallised salt sparingly in boiling absolute alcohol, which abstracts the water, and leaves the greater part of the salt in the form of a resinous mass. (Corriol.) Phosphoric acid precipitates phosphate of lime from the alcoholic solution of the salt, and, nevertheless, aqueous lactic acid dissolves phosphate of lime (Pelouze), even the dilute acid dissolving it readily. (Cap & Henry.) Oxalate of lime likewise dissolves to a certain extent in lactic acid. (Cap & Henry.) Aqueous lactate of lime mixed with sulphates yields a deposit of gypsum only on boiling.

| *Dehydrated at* 100°. | | | Engelhardt & Maddrell. |
|---|---|---|---|
| 12 C | 72 | 33·03 | 32·67 |
| 10 H | 10 | 4·59 | 4·72 |
| 2 CaO | 56 | 25·69 | 25·56 |
| 10 O | 80 | 36·69 | 37·05 |
| $C^{12}H^{10}Ca^2O^{12}$ | 218 | 100·00 | 100·00 |

| *Air-dried crystals.* | | |
|---|---|---|
| 12 C | 72 | 23·37 |
| 20 H | 20 | 6·50 |
| 2 CaO | 56 | 18·18 |
| 20 O | 160 | 51·95 |
| $C^{12}H^{10}Ca^2O^{12} + 10Aq$ | 308 | 100·00 |

The crystallised salt, $C^{12}H^{10}Ca^2O^{12} + 10$ Aq. contains 29·17 p. c. water (Wackenroder); 29·22 (Engelhardt & Maddrell); 29·4 (Corriol); 29·5 (Gay-Lussac & Pelouze.)

*b. Monobasic.* — 1 pt. of the acid saturated with carbonate of lime is mixed with at least 1 pt. more of the free acid, and the liquid evaporated to a syrup. If sufficient acid be not added, the salt *a* crystallises out at first. Concentrically fibrous crystalline masses resembling wavellite; from the solution in boiling absolute alcohol, the salt separates in the form of a crystalline web, which may be freed from adhering acid by washing with ether. After drying in the air, it is soft to the touch, permanent in the air, gives off 8·8 p. c. (2 At.) water of crystallisation at 80°, and 0·36 p. c. more at 90°, with slight contraction and empyreumatic odour. (Engelhardt & Maddrell.)

| *At* 80°. | | | Engelhardt & Maddrell. |
|---|---|---|---|
| 12 C | 72 | 36·18 | 36·20 |
| 11 H | 11 | 5·53 | 5·81 |
| CaO | 28 | 14·07 | 14·01 |
| 11 O | 88 | 44·22 | 43·98 |
| $C^{12}H^{11}CaO^{12}$ | 199 | 100·00 | 100·00 |

*Chloride of Calcium with Lactate of Lime.* — The prisms obtained by evaporating an aqueous solution of lactate of lime with excess of chloride of calcium, are dried between paper, and washed with cold ordinary alcohol. The prisms, which are different from those of hydrated chloride of calcium, leave, at each crystallisation from water, a portion of chloride of calcium in the mother-liquor. At 110°, they give off 22·13 per cent. (rather more than 6 At. of water). They dissolve very readily in cold water and in ordinary or absolute alcohol at the boiling heat, but with difficulty in cold alcohol. (Engelhardt & Maddrell.)

| *Dried at* 100°. | | | Engelhardt & Maddrell. |
|---|---|---|---|
| 12 C | 72 | 20·76 | 21·14 |
| 12 H | 12 | 3·46 | 3·45 |
| 4 CaO | 112 | 32·30 | 32·55 |
| 2 Cl | 70·8 | 20·41 | 20·75 |
| 10 O | 80 | 23·07 | 22·11 |
| $2CaCl,C^{12}H^{10}Ca^{2}O^{12} + 2Aq$ | 346·8 | 100·00 | 100·00 |

*Lactate of Lime and Potash.* — When one-half of an aqueous solution of lactate of lime is precipitated by carbonate of potash, the other half then added, and the liquid evaporated over the water-bath, a syrupy mass is obtained, which when further heated, gradually changes to a mass of transparent, granular crystals. If an excess of carbonate of potash is used, the granules are larger, but part of the liquid refuses to crystallise. The uncrystallisable syrup may however be removed by rapid washing with cold water, and crystals are then obtained, 1 or 2 lines in length and apparently octohedrons belonging to the oblique prismatic system. The hard colourless grains dissolve in water slowly in the cold, easily when heated; from a concentrated solution, the double salt crystallises out unaltered, whereas a dilute solution deposits lactate of lime. The crystals do not suffer any diminution of weight at 120°; at a higher temperature, they melt without decomposition, and solidify in a vitreous mass on cooling. (Strecker, *Ann. Pharm.* 81, 248; 91, 352.)

| | | | Strecker. |
|---|---|---|---|
| $C^{12}H^{10}O^{10}$ | 162·0 | 68·3 | 68·3 |
| CaO | 28·0 | 11·8 | 11·2 |
| KO | 47·2 | 19·9 | 20·5 |
| $C^{12}H^{10}KCaO^{12}$ | 237·2 | 100·0 | 100·0 |

*Lactate of Lime and Soda.* — Prepared like the potash-salt. Crystallises from the concentrated solution on cooling in colourless, transparent, hard granules, which give off water and become opaque at 100°, and melt at a higher temperature. The salt dried over oil of vitriol gives off 8·1 p. c. (2 At.) water at 130.° (Strecker.)

| *Dried at* 130°. | | | Strecker. |
|---|---|---|---|
| $C^{12}H^{10}O^{10}$ | 162·0 | 73·2 | 73·6 |
| CaO | 28·0 | 12·7 | 12·6 |
| NaO | 31·2 | 14·1 | 13·8 |
| $C^{12}H^{10}NaCaO^{12}$ | 221·2 | 100·0 | 100·0 |

| *Dried over oil of vitriol.* | | | Strecker. |
|---|---|---|---|
| $C^{12}H^{10}NaCaO^{12}$ | 221·2 | 92·5 | 91·9 |
| 2 HO | 18·0 | 7·5 | 8·1 |
| $C^{12}H^{10}NaCaO^{12}$ + 2Aq | 239·2 | 100·0 | 100·0 |

*Bibasic Lactate of Magnesia.* — The boiling aqueous acid is saturated with carbonate of magnesia, or sulphate of magnesia is precipitated by lactate of baryta, and the filtrate evaporated. Crystalline crusts and shining prisms, perfectly neutral, not efflorescing excepting in vacuo over oil of vitriol; at 100° they give off 21·12 p. c. (6 At.) water. (Engelhardt & Maddrell.) By slow evaporation, granular crystals are obtained; by quick evaporation, a transparent gum. (Berzelius.) Granular, somewhat efflorescent crystals, having a slight taste and charring without fusion when heated. (Braconnot.) Shining efflorescent crystals. (Gay-Lussac & Pelouze.) When the solution is evaporated over the water-bath, an anhydrous salt is obtained having a silky lustre. (Engelhardt & Maddrell.) The ordinary crystals dissolve in 25 pts. of cold water (Braconnot), in 28 pts. of cold and in 6 pts. of boiling water, but not in alcohol either hydrated or absolute, even when heated (Engelhardt & Maddrell); in 30 pts. of cold water. (Gay-Lussac & Pelouze.)

| *Dried at* 100. | | | Engelhardt & Maddrell. |
|---|---|---|---|
| 12 C | 72 | 35·64 | 35·45 |
| 10 H | 10 | 4·95 | 4·98 |
| 2 MgO | 40 | 19·81 | 20·00 |
| 10 O | 80 | 39·60 | 39·57 |
| $C^{12}H^{10}Mg^2O^{12}$ | 202 | 100·00 | 100·00 |

*Lactate of Magnesia and Ammonia.* — When lactate of magnesia is precipitated by excess of ammonia, and the filtrate evaporated, needles are obtained which are permanent in the air. (Berzelius.)

*Lactate of Alumina.* — Hydrate of alumina is scarcely soluble in the acid. By precipitating lactate of baryta with sulphate of alumina, a filtrate is obtained, which contains a large quantity of alumina, but does not yield any crystals. (Engelhardt & Maddrell). — Gum permanent in the air. (Braconnot.)

*Chromic Lactate.* — Hydrated chromic oxide dissolves very easily in lactic acid, forming a liquid, which, when evaporated yields a syrup but no crystals. (Gay-Lussac & Pelouze; Engelhardt & Maddrell.)

*Uranic Lactate.* — The base obtained by heating uranic nitrate and boiling with water, dissolves readily in the acid, and yields by evaporation and cooling, a syrup, and afterwards, light yellow crystalline crusts which redden litmus strongly. They give off only 1 per cent. of water, probably hygroscopic, at 100°, and glow when more strongly heated in contact with the air. They dissolve readily in water, their solution acquires a green colour by exposure to the sun and afterwards deposits a brown oxide free from lactic acid. (Engelhardt & Maddrell.)

| | *Crystals at* 100°. | | Engelhardt & Maddrell. |
|---|---|---|---|
| 12 C | 72 | 16·00 | 15·89 |
| 10 H | 10 | 2·22 | 2·27 |
| 2 $U^2O^3$ | 288 | 64·00 | 63·46 |
| 10 O | 80 | 17·78 | 18·38 |
| $C^{12}H^{10}(U^2O^2)O^{12}$ | 450 | 100·00 | 100·00 |

*Lactate of Manganese.* — By boiling carbonate of manganese with the acid. Rectangular prisms bevelled with two faces resting on the narrow lateral faces; somewhat efflorescent; melt in their water of crystallisation when heated. (Braconnot.) By rather quick evaporation, highly lustrous crystalline crusts are obtained, sometimes colourless, sometimes of a pale rose colour; by spontaneous evaporation, large crystals belonging to the right prismatic system and agreeing in form with those of the copper-salt. (Engelhardt & Maddrell; *comp.* Ettling, *Ann. Pharm.* 63, 108.) They are permanent in the air, give off 9·66 per cent. of water when placed over oil of vitriol in the air, apparently 4 At. over oil of vitriol in vacuo, and 18·69 p. c. (6 At.) at 100°. (Engelhardt & Maddrell.) The crystals are colourless or pale rose-coloured, efflorescent, and contain 10 At. water. (Gay-Lussac & Pelouze.) — They dissolve in 12 pts. of cold water (Braconnot); more readily in boiling water; are insoluble in ordinary alcohol when cold, but dissolve in it with tolerable facility at the boiling heat; alcohol also throws down the aqueous solution, crystals of different appearance but containing the same amount of water. (Engelhardt & Maddrell.)

| | *At* 100°. | | Engelhardt & Maddrell. |
|---|---|---|---|
| 12 C | 72 | 30·77 | 30·61 |
| 10 H | 10 | 4·27 | 4·31 |
| 2 MnO | 72 | 30·77 | 30·56 |
| 10 O | 80 | 34·19 | 34·52 |
| $C^{12}H^{10}Mn^2O^{12}$ | 234 | 100·00 | 100·00 |

Antimonic oxide, even that which is precipitated from tartar-emetic by ammonia (Lepage. *J. chim. méd.* 20, 8), is nearly insoluble in lactic acid, but dissolves somewhat copiously in acid lactate of potash, without however yielding crystals (Engelhardt & Maddrell). *Biantimoniate* of potash dissolves with tolerable facility in lactic acid. (J. O. Buchner.)

*Lactate of Bismuth.* — *a. Bibasic.* — Nitric acid saturated with bismuth is dropped into a dilute solution of lactate of soda; the mixture boiled for some time; and the copious precipitate collected in a filter, and washed with water. Dried at 100°, at which temperature it does not diminish in weight, it contains 74·55 per cent. of teroxide of bismuth, so that its formula is $2BiO^3,C^{12}H^{10}O^{10}$. It is neither dissolved nor decomposed by water, either cold or boiling. (Engelhardt & Maddrell.)

*b. Monobasic.* — The hydrate or carbonate of teroxide of bismuth dissolves sparingly in the acid, and yields by evaporation small crystals, which when purified from the free acid by washing with alcohol and afterwards with ether, present the appearance of delicate microscopic needles. — 2. Nitric acid saturated with bismuth is precipitated by a slight excess of concentrated solution of lactate of soda; the resulting crystalline magma of lactate of bismuth and nitrate of soda dissolved in the smallest possible quantity of [warm ?] water, which takes place without turbidity, if the nitrate of bismuth is not in excess; the solution left at rest; the mother-liquor, after separation from the resulting crystalline crusts, mixed with alcohol, till it begins to be milky; separated after two days from the newly formed crusts; and the addition of alcohol in small quantity repeated as often as crystalline crusts are obtained; these crusts are then rinsed with the smallest possible quantity of water, and dried in the air. If too much alcohol were added at once, nitrate of soda would be likewise precipitated, and this could be washed away without some decomposition of the bismuth-salt. — The crusts do not give off any thing at 100°. They impart to cold water, a certain portion of acid, together with a trace of teroxide; but they dissolve for the most part in boiling water, leaving the salt *a*, and the solution, on cooling does not yield any crystals; when evaporated however, it deposits crystalline crusts [of a more acid salt ?], which form a clear solution with a small quantity of water, but produce considerable turbidity with a larger quantity. (Engelhardt, *Ann. Pharm.* 651, 367.)

| *At* 100°. | | | Engelhardt. |
|---|---|---|---|
| 12 C | 72 | 18·18 | 19·33 |
| 10 H | 10 | 2·53 | 2·55 |
| $BiO^3$ | 234 | 59·09 | 59·15 |
| 10 O | 80 | 20·20 | 18·97 |
| $BiO^3,C^{12}H^{10}O^{11}$ | 396 | 100·00 | 100·00 |

[The result of the analysis does not appear to be reconcilable with the nucleus-theory.]

*Lactate of Zinc.*—Obtained by dissolving the carbonate in lactic acid, or by mixing lactate of lime with chloride of zinc, and washing the small crystals (Blücher, *Pogg.* 63, 429); or again, by a process similar to Wöhler's method of preparing the iron-salt (p. 491.) Crystallises readily. Small, obliquely truncated, four-sided prisms (Braconnot, Gay-Lussac &

Pelouze); belonging to the right prismatic system. (K. Schmidt, *Ann. Pharm.* 61, 331; *vid.* also Schabus, *Jahresber.* 1854, 405). Needles having a slightly acid, styptic taste. (Cap & Henry.) Needles which redden litmus. (Engelhardt & Maddrell.) The crystals give off 17·79 per cent. (6 At.) water at 100°. (Mitscherlich & Liebig, *Ann. Pharm.* 7, 47.) They do not lose weight over oil of vitriol in the air; but in vacuo, they give off 18·22 p. c. water, so that from 120° to 160°, they lose only 3·184 per cent. and no more at 310°. (Engelhardt & Maddrell.) A further loss takes place at 250°, but the salt turns brown at the same time. (Gay-Lussac & Pelouze.) At a higher temperature, charring and combustion takes place, but without fusion. Sulphuretted hydrogen does not completely precipitate the zinc from the aqueous solution [?]. (Braconnot; compare p. 476). The crystals dissolve in more than 50 pts. of cold water, in a smaller quantity of hot water (Braconnot); in 58 pts. of cold, and in 6 pts. of boiling water (Engelhardt & Maddrell). The salt is nearly insoluble (quite, according to Gay-Lussac & Pelouze) in alcohol either cold or boiling. (Cap & Henry; Engelhardt & Maddrell.)

| | | | Mitscherlich & Liebig. | Engelhardt & Maddrell. | Strecker. | Heintz. |
|---|---|---|---|---|---|---|
| 12 C | 72·0 | 29·70 | 29·34 | 29·55 | 29·43 | 29·61 |
| 10 H | 10·0 | 4·13 | 4·22 | 4·08 | 4·18 | 4·19 |
| 2 ZnO | 80·4 | 33·17 | 33·26 | 33·48 | 33·10 | 33·34 |
| 10 O | 80·0 | 33·00 | 33·18 | 32·89 | 33·29 | 32·86 |
| $C^{12}H^{10}Zn^{2}O^{12}$ | 242·4 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 |

| *Crystals.* | | | Mitscherlich & Liebig. | | Thomson. |
|---|---|---|---|---|---|
| 12 C | 72·0 | 24·29 | 24·04 | | 24·72 |
| 16 H | 16·0 | 5·40 | 5·49 | | 5·41 |
| 2 ZnO | 80·4 | 27·13 | 27·29 | | 26·89 |
| 16 O | 128·0 | 43·18 | 43·18 | | 42·98 |
| $C^{12}H^{10}Zn^{2}O^{12}$ + 6Aq | 296·4 | 100·00 | 100·00 | | 100·00 |

The salt analysed by Strecker was prepared from alanine (ix, 434); Thomson's crystals (*Ann. Pharm.* 23, 238) were obtained from the acid of sauerkraut.

*Lactate of Zinc and Potassium.* — Prepared like the corresponding sodium-salt;—after drying over oil of vitriol, it is anhydrous. (Strecker.)

*Lactate of Zinc and Sodium.* — By partially precipitating lactate of zinc with carbonate of soda, and evaporating over the water-bath, a syrupy residue is obtained, which on cooling solidifies for the most part into a rather soft crystalline mass. After drying over oil of vitriol, it gives off 9·0 p. c. (2 At.) water at 120°. Dissolves readily in water, but a moderately dilute solution yields crystals of lactate of zinc. (Strecker, *Ann. Pharm.* 91, 354.)

| *Dried at* 120°. | | | Strecker. |
|---|---|---|---|
| $C^{12}H^{10}O^{10}$ | 162·0 | 69·4 | |
| ZnO | 40·2 | 17·2 | 17·2 |
| NaO | 31·2 | 13·4 | |
| $C^{12}H^{10}ZnNaO^{12}$ | 233·4 | 100·0 | |

*Lactate of Cadmium.* — 1. Obtained by dissolving the hydrate or carbonate of the oxide in the boiling acid to saturation, then filtering, evaporating till a crystalline film forms, and cooling. (Lepage, *J. chim. méd.* 20, 8; also *J. pr. Chem.* 31, 377; Engelhardt & Maddrell.) — 2. By mixing the boiling solutions of lactate of lime and sulphate of cadmium in exactly equivalent proportions, filtering from sulphate of lime and evaporating. (Lepage.) — Spongy mass consisting of small white needles (Lepage); colourless neutral needles, which, after drying in the air, give off only 0·28 p. c. of hygroscopic water at 100°. (Engelhardt & Maddrell.) — The salt dissolves in 8 or 9 pts. of cold. and in 4 pts. of boiling water, but does not crystallise from the latter solution on cooling, unless it be previously evaporated till a crystalline film forms. (Lepage.) Dissolves in 10 pts. of cold and in 8 pts. of boiling water, but not in alcohol even when hot. (Engelhardt & Maddrell.)

| *Needles.* | | | Engelhardt & Maddrell. |
|---|---|---|---|
| 12 C | 72 | 24·83 | 24·72 |
| 10 H | 10 | 3·45 | 3·43 |
| 2 CdO | 128 | 44·14 | 43·88 |
| 10 O | 80 | 27·58 | 27·97 |
| $C^{12}H^{10}Cd^2O^{12}$ | 290 | 100·00 | 100·00 |

*Stannous Lactate.* — *Quadrobasic.* — The acid solution of protochloride of tin mixed with bibasic lactate of soda, deposits a white crystalline powder, which must be washed with water. After drying in the air, it gives off only 0·77 per cent. of water at 100°; is insoluble in cold water and alcohol; gives up to boiling water a large quantity of acid and a trace of tin, dissolves readily in hydrochloric acid, and also in acetic acid after boiling for some time. (Engelhardt & Maddrell.) The solution of tin in lactic acid deposits a certain quantity of binoxide when evaporated, and afterwards deposits an acid salt in small wedge-shaped octohedrons. (Braconnot.)

| *Crystals at* 100°. | | | Engelhardt & Maddrell. |
|---|---|---|---|
| 12 C | 72 | 16·74 | 17·06 |
| 10 H | 10 | 2·33 | 1·96 |
| 4 SnO | 268 | 62·33 | 63·34 |
| 10 O | 80 | 18·60 | 17·64 |
| $2SnO,C^{12}H^{10}Sn^2O^{10}$ | 430 | 100·00 | 100·00 |

*Stannic Lactate.* — Bichloride of tin does not form a precipitate with lactate of soda; nor does the mixture yield crystals when evaporated to a syrup. (Engelhardt & Maddrell.)

*Lactate of Lead.* — *Polybasic.* — By digesting *b* with oxide of lead, which then swells up considerably, or by precipitating it with a small quantity of ammonia. The mass when dissolved in water, has an alkaline reaction and a styptic taste. It dries up to a soft powder; glimmers away like tinder, when set on fire at a single point, leaving about 83 per cent. of lead with a small quantity of oxide; and dissolves sparingly in cold, more freely in hot water, whence on cooling, a portion is deposited in the

form of a light yellow powder; the solution is clouded by the carbonic acid of the air. (Berzelius.)

*b. Bibasic?* — By saturating the boiling acid with carbonate of lead. The sweet and styptic-tasting syrup obtained by evaporation dries up to an easily soluble gum (Scheele, Braconnot), and forms after standing for some time, a granular salt, permanent in the air, soluble in alcohol. (Berzelius.) The acid saturated while hot with carbonate of lead, is neutral, but when exposed to the air, becomes slightly acid, in consequence of the formation of a film of carbonate of lead; over oil of vitriol, it dries up to a gum which dissolves easily in ordinary alcohol, but is insoluble in absolute alcohol when cold, and very sparingly soluble at the boiling heat; from the hot alcoholic solution, it separates completely in threads on cooling; ether does not dissolve a trace of it. (Engelhardt & Maddrell.)

*Ferrous Lactate.* — 1. Obtained by dissolving iron filings in the hot aqueous acid as long as hydrogen continues to escape, and filtering the liquid while hot (Braconnot, Gay-Lussac & Pelouze).—Kossmann (*Repert.* 77, 226) washes the crystals obtained from the filtrate by cooling, on the filter, first with a small quantity of cold water, then with alcohol. He likewise obtains an additional quantity of crystals from the mother-liquor by boiling with iron filings. (Compare Louradour, *J. Pharm.* 26, 165.) — 2. By dissolving ferrous carbonate in lactic acid. Lipowitz (*N. Br. Arch.* 32, 277) precipitates ferrous sulphate purified by Bonsdorff's process (v, 238) with carbonate of soda at the boiling heat; washes the precipitate quickly with boiling alcohol; dissolves it in previously heated lactic acid; and quickly dries between paper the crystals which form on cooling. — 3. Bibasic lactate of ammonia, soda, lime or baryta is precipitated by ferrous sulphate or chloride (Lepage, *J. Chim. méd.* 22, 5): The solution of 100 pts. of lactate of lime in 500 pts. of boiling water, is mixed in a flask with a solution of 62 pts. ferrous sulphate in 500 pts. of water and a small quantity of lactic acid; the mixture heated with agitation in the water-bath; the solution quickly filtered from the gypsum, and rapidly boiled down to one-half in contact with a small quantity of iron wire in a porcelain or cast iron vessel; the liquid filtered; the crystals which form on cooling washed with alcohol and dried between paper; and the mother-liquor repeatedly evaporated to the crystallising point.—A similar process is adopted by Wackenroder. — Engelhardt & Maddrell: Oil of vitriol is boiled in a flask with excess of lactate of baryta; the filtrate mixed with alcohol, and the crystals washed with that liquid.—Haidler (*Jahrb. pr. Pharm.* 9, 20): Alcoholic solutions of lactate of lime and protochloride of iron are mixed, and the resulting crystals washed with alcohol after 24 hours. — Blücher (*Pogg.* 63, 429): Aqueous solutions of the two salts. — Wackenroder: 194 pts. of lactate of lime dissolved in the smallest possible quantity of boiling water, are added to a saturated solution of 34 pts. of iron in hydrochloric acid; the mixture set aside to crystallise in a closed vessel completely filled with it; and the remainder of the crystals precipitated from the mother-liquor by addition of alcohol free from air.— Pagenstecher (*Repert.* 76, 307): Lactate of ammonia (obtained by precipitating lactate of lime with carbonate of ammonia and evaporating the filtrate to a syrup) dissolved in 6 pts. of alcohol of 30° Bm., is mixed with a concentrated solution of protochloride of iron; and the crystals which form in 36 hours, collected upon linen, washed with alcohol, pressed

between paper, and dried at a gentle heat, or better in vacuo over oil of vitriol. Engelhardt & Maddrell recrystallise the salt thus obtained from water free from air.

4. This salt is also formed when sugar of any kind is left to undergo the lactic acid fermentation in contact with iron filings. — Wöhler (*Ann. Pharm.* 48, 149): 2 lbs. of sour milk, with 1 oz. of milk-sugar and 1 oz. of iron filings, are set aside for several days at a temperature between 30° and 40°, the mixture being shaken and the milk-sugar renewed from time to time, till the ferrous lactate is deposited in the form of a white crystalline powder. The liquid is then heated to the boiling point, filtered hot into a vessel which is afterwards closed, the mother-liquor, after a few days, poured off from the crust of needle-shaped crystals; and these crystalline crusts washed with cold water, and quickly dried on bibulous paper at a gentle heat, or previously recrystallised from boiling water. (Compare Gobley, *N. J. Pharm*, 6, 57; Ruder, *Jahrb. pr. Pharm.* 6, 45.)

Yellowish white needles, which redden litmus and are permanent in the air after drying. (Engelhardt & Maddrell.) Greenish white crusts and grains made up of slender rectangular needles, having a sweetish ferruginous taste, and permanent in the air. (Wittstein, *Repert.* 83, 171.) White tabular crystals, which redden litmus. (Louradour.) — The needles give off all their water, amounting to 19·13 p. c. (6 At.) in vacuo, or when heated to 100° in a stream of hydrogen. At 60° in the air, they give off water and turn brown, then gradually black, being nearly transformed into ferric lactate which is easily soluble in water, and gives off an empyreumatic odour at 120°. (Engelhardt & Maddrell.) The needles swell up slightly when heated in contact with the air, give off white acid vapours smelling like burnt tartar, and finally leave 27·1 p. c. of ferric oxide. The aqueous solution oxidises quickly in contact with the air, turning brown, but without forming a precipitate. (Engelhardt & Maddrell.) When boiled in a narrow-necked flask, it acquires a brownish yellow colour, in a few minutes, even before any ferric salt is formed, and becomes turbid by continued boiling, in consequence of the precipitation of hydrated ferric oxide, amounting in the end to 7·5 per cent. while the iron which remains dissolved in the brownish yellow, strongly acid liquid is also in the end completely converted into ferric oxide,—and the liquid, if subsequently digested with iron filings, takes up a small quantity of iron, but retains its yellow colour, and again deposits ferric oxide when boiled. The formation of ferric oxide during the boiling appears to be accompanied by an alteration and colouring of the acid. The aqueous solution of the needles heated in shallow dishes, dries up without turbidity to a dingy yellow-green, transparent, brittle mass of resin, containing both protoxide and sesquioxide of iron; deliquesces to a syrup on exposure to the air; and dissolves completely in water. (Wittstein.)

The needles dissolve in 48 pts. of water at 10°, forming a pale yellow-green solution; in 12 pts. of boiling water; very sparingly in weak, and not at all in strong alcohol. (Wittstein.) They dissolve with tolerable facility in boiling alcohol. (Engelhardt & Maddrell.)

The salt may be contaminated with ferrous sulphate (to be detected by chloride of barium), with starch (by iodine), with milk-sugar (by boiling with 15 pts. of nitric acid to 3 pts. of the salt, and crystallising the resulting mucic acid by cooling). (Louradour.) — Ferrous sulphate mixed with a sufficient quantity of lactic acid, is not precipitated by ammonia, not even after continued exposure to the air and heating.

| | *Dried at* 100°. | | Engelhardt & Maddrell. |
|---|---|---|---|
| 12 C | 72 | 30·77 | 30·46 |
| 10 H | 10 | 4·27 | 4·29 |
| 2 FeO | 72 | 30·77 | 30·45 |
| 10 O | 80 | 34·19 | 34·80 |
| $C^{12}H^{10}Fe^2O^{12}$ | 234 | 100·00 | 100·00 |

*Ferric Lactate.*—After evaporation of the solution. Brown mass. (Braconnot, Gay-Lussac and Pelouze), red-brown (Berzelius), yellow amorphous (Engelhardt & Maddrell), deliquescent (Gay-Lussac & Pelouze), insoluble in alcohol. (Berzelius.)—The dark-yellow solution of recently precipitated ferric hydrate in the heated acid, which is completely precipitable by ammonia, and in which the merest trace of protoxide of iron, formed at the expense of the acid, may be detected, yields by evaporation a yellowish green resinous mass, in which about $\frac{1}{7}$ of the iron appears to be converted into protoxide.—Sesquichloride of iron mixed with a large quantity of lactic acid, assumes a dark red colour when mixed with ammonia in the cold, and forms after some minutes only, a brownish precipitate, a small quantity of iron remaining in solution; but when heated, it immediately deposits nearly all the iron. (Wittstein.)

*Lactate of Cobalt.*—By boiling the hydrate with the acid. (Engelhardt and Maddrell.) Rose-coloured crystalline grains (Braconnot, Gay-Lussac & Pelouze), consisting of needles, slightly acid and permanent in the air; they do not give off anything in vacuo over oil of vitriol, but at 100°, they part with all their water, amounting to 19·58 per cent. (Engelhardt & Maddrell.) In the fire, they char and burn, but do not melt. Sulphuretted hydrogen precipitates from their aqueous solution only a portion of the oxide, leaving a pale red [monobasic ?] salt. (Braconnot.) The grains dissolve in 38 pts. of cold water (Braconnot), more readily in boiling water, but are insoluble in alcohol which precipitates them from water. (Engelhardt & Maddrell.)

| | *Dried at* 100°. | | Engelhardt & Maddrell. |
|---|---|---|---|
| 12 C | 72 | 30·38 | 30·36 |
| 10 H | 10 | 4·22 | 4·46 |
| 2 CoO | 75 | 31·65 | 31·49 |
| 10 O | 80 | 33·75 | 33·69 |
| $C^{12}H^{10}Co^2O^{12}$ | 237 | 100·00 | 100·00 |

*Lactate of Nickel.*—By dissolving carbonate of nickel in the boiling acid, or by precipitating the sulphate with lactate of baryta, and filtering. (Engelhardt & Maddrell.) Emerald-green, indistinct crystals, having a sweet and afterwards metallic taste. (Braconnot.) Small apple-green needles, or from very concentrated solutions, crystalline crusts, which redden litmus slightly, and are permanent in the air. In vacuo over oil of vitriol, it gives off a tolerably large quantity of water, at 100°, 11·42 per cent. (4 At.), and at 130°, in all 18·39 p. c. (6 At.) (Engelhardt & Maddrell). Chars and inflames in the fire, but without fusing; dissolves in 30 pts. of cold water (Braconnot), more easily in boiling water, and is insoluble in alcohol, even when hot, which, in fact, precipitates it from the aqueous solution in the form of a pulp soon becoming crystalline. (Engelhardt and Maddrell.)

| *Dried at* 100°. | | | Engelhardt & Maddrell. |
|---|---|---|---|
| 12 C | 72 | 28·23 | 27·56 |
| 12 H | 12 | 4·71 | 4·79 |
| 2 NiO | 75 | 29·41 | 29·18 |
| 12 O | 96 | 37·65 | 38·47 |
| $C^{12}H^{10}Ni^2O^{12}$ + 2Aq | 255 | 100·00 | 100·00 |

*Cupric Lactate.* — *a. Quadrobasic.* — Lactic acid saturated at the boiling heat with cupric carbonate, deposits on cooling a light blue mixture of a heavy granular salt *a*, and another pasty basic salt, from which the former may be separated by levigation.

The latter salt dissolves very sparingly, even in boiling water; it cannot be obtained quite pure, and accordingly gives, sometimes 45·16 per cent. of cupric oxide and 13·97 water, sometimes 45·71 cupric oxide and 15·47 water.

The salt *a* presents the appearance of dark blue heavy granules, also sparingly soluble in water. (Engelhardt & Maddrell.)

| *a. Dried at* 100°. | | | Engelhardt & Maddrell. |
|---|---|---|---|
| 12 C | 72 | 22·36 | 22·44 |
| 10 H | 10 | 3·11 | 2·96 |
| 4 CuO | 160 | 49·69 | 49·89 |
| 10 O | 80 | 24·84 | 24·71 |
| $2CuO,C^{12}H^{10}Cu^2O^{12}$ | 322 | 100·00 | 100·00 |

*b.* — *Bibasic.* — Cuprous oxide in contact with lactic acid, yields metallic copper and cupric lactate. (Gay-Lussac & Pelouze.) — 1. By boiling carbonate of copper with a larger quantity of the acid. — 2. By precipitating lactate of baryta with sulphate of copper. — On evaporating and cooling the filtrate, the salt is obtained in large crystals (Engelhardt & Maddrell); sometimes in blue right rectangular prisms, sometimes, though more rarely, in thick dark green prisms, which pass into the blue when recrystallised. Both kinds of crystals contain 4 At. water. (Pelouze.) The green crystals are flat prisms belonging to the oblique prismatic system, and resembling gypsum. The crystals run through all shades of colour, between blue and green, and the green crystals are produced in greatest abundance by the second mode of preparation, and do not turn blue by recrystallisation. Alcohol, added to the aqueous solution, throws down light blue silky needles of the same composition. — The crystals give off all their water, amounting to 13·13 per cent. (4 At.) in cold air over oil of vitriol, and very quickly at 100°, without change of appearance. The dry salt remains unaltered up to 200°, and burns away with a glimmering light at 210°. (Engelhardt & Maddrell.) When subjected to dry distillation, it melts, gives off 26·2 per cent. of carbonic oxide and carbonic acid, yields 41 per cent. of a distillate similar to that obtained with the free acid (the last third, which is a solution of lactide in acetone, immediately solidifying as lactide on addition of water), and leaves 29·5 p. c. copper with 3·3 charcoal. (Pelouze.) The dry salt yields between 200° and 210°, carbonic acid, aldehyde, and a certain quantity of ordinary lactic acid (perhaps arising from a residue of water in the salt), and leaves copper together with lactic anhydride, which decomposes between 250° and 260°, as described at page 480. (Engelhardt, *Ann. Pharm.* 70, 241.) — The

aqueous solution forms with excess of potash, a clear dark blue liquid, and with excess of lime, a liquid of a lighter blue colour, with partial precipitation of the oxide. (Pelouze.) In this respect, lactic acid agrees with the sugars, and differs from acetic, tartaric, racemic, and citric acid, from which oxide of copper may be completely precipitated by lime. (Pelouze.) But if sufficient milk of lime be present, the hydrated cupric oxide, which at first dissolves in the lactate of lime, is completely precipitated; and from cupric nitrate containing sal-ammoniac, glycocol, gelatin,—or more especially, gelatin, casein or fibrin mixed with potash, milk of lime does not precipitate the cupric oxide completely; only impure lactate of lime, not lactate of zinc, protects cupric nitrate from complete precipitation. Hence this reaction given by Pelouze, as a test of the presence of lactic acid in the gastric juice, in cows' urine, and in the yolk of egg (p. 473), requires fuller confirmation. (Strecker, *Ann. Pharm.* 62, 216.)

The crystals dissolve in 6 pts. of cold water, in 2·2 pts. of boiling water, in 115 pts. of cold and in 26 pts. of boiling alcohol. (Engelhardt & Maddrell.)

| *Dried at* 100°. | | | Engelhardt & Maddrell. |
|---|---|---|---|
| 12 C | 72 | 29·75 | 29·64 |
| 10 H | 10 | 4·14 | 4·14 |
| 2 CuO | 80 | 33·06 | 32·27 |
| 10 O | 80 | 33·05 | 33·95 |
| $C^{12}H^{10}Cu^2O^{12}$ | 242 | 100·00 | 100·00 |

*Mercurous Lactate.*—Needles which, when heated, melt in their water of crystallisation, froth up, assume an olive-green colour, emit the odour of acetic acid, and leave charcoal mixed with mercury. Dissolves readily in water. (Braconnot.) A mixture of 1 vol. warm, highly concentrated lactate of soda and 2 vol. of a saturated solution of mercurous nitrate, soon deposits a small quantity of mercury and assumes a rose or carmine colour, and then, after 24 hours, yields rose or carmine-coloured laminæ grouped in rosettes. These crystals give off 5·64 p. c. (4 At.) water at 100°, becoming darker in colour, but without further decomposition. They dissolve sparingly in cold water, forming a very acid liquid, and when immersed in boiling water, are resolved into metallic mercury and a mercuric salt. They are insoluble in cold alcohol, and their solution in boiling alcohol deposits a white heavy powder. (Engelhardt & Maddrell.)

| *Air-dried crystals.* | | | Engelhardt & Maddrell. |
|---|---|---|---|
| 12 C | 72 | 12·08 | 12·49 |
| 10 H | 10 | 1·68 | |
| 4 Hg | 400 | 67·11 | 67·44 |
| 12 O | 96 | 16·11 | |
| 2 HO | 18 | 3·02 | |
| $C^{12}H^{10}Hg^4O^{12}$ + 2Aq | 596 | 100·00 | |

*Mercuric Lactate.*—*Quadribasic.*—By saturating the boiling dilute acid with mercuric oxide, filtering, evaporating to a syrup, and cooling, a mixture is obtained of a small quantity of light yellow insoluble powder,

and a large quantity of a colourless easily soluble powder; and this, when exhausted with boiling water, yields a solution whence the salt is deposited in shining needles which redden litmus strongly. These needles do not suffer any loss at 100°; they dissolve very readily in cold water, are not decomposed by boiling with water, and dissolve with difficulty in alcohol even when hot. (Engelhardt & Maddrell.) — Red deliquescent gum which after some weeks deposits a semi-crystalline powder. (Berzelius.)

| *Crystals.* | | | Engelhardt & Maddrell. |
|---|---|---|---|
| 12 C | 72 | 12·12 | 12·41 |
| 10 H | 10 | 1·68 | |
| 4 Hg | 400 | 67·34 | 67·61 |
| 14 O | 112 | 18·86 | |
| $2HgO,C^{12}H^{10}Hg^2O^{12}$ | 594 | 100·00 | |

*Lactate of Silver.* — *Bibasic.* — Obtained by saturating the aqueous acid with oxide of silver. White, very slender needles, having a silky lustre, and united in tufts (in nodules, according to Engelhardt & Maddrell). They assume a reddish colour on exposure to light (blackish, especially when heated, and give off 8·34 per cent. (4 At.) water at 80°). (Engelhardt & Maddrell.) They melt quickly when heated, turning brown and swelling up (at 100°, with blackening, according to Engelhardt & Maddrell), then take fire and leave silver mixed with charcoal. (Braconnot.) Their aqueous or alcoholic solution is decolorised by continued boiling, and gradually deposits brown flakes. (Engelhardt & Maddrell.) They dissolve in 20 pts. of cold water (Braconnot); are nearly insoluble in cold alcohol; but dissolve so abundantly in hot alcohol that the solution solidifies in a crystalline pulp on cooling. From the cooled solution, ether precipitates the remainder of the salt, producing at the same time, a strong blue colour. (Engelhardt & Maddrell.) Acetate of potash added to the aqueous solution throws down acetate of silver. (Gay-Lussac & Pelouze.) — The solution of the oxide in the aqueous acid dries up to a soft translucent gum, which has a sharp metallic taste, and whose alcoholic solution becomes greenish yellow by evaporation, and when redissolved in water, deposits brown argentiferous flakes and assumes a red colour. (Berzelius.)

| *Dried at* 80°. | | | Engelhardt & Maddrell. |
|---|---|---|---|
| 12 C | 72 | 18·27 | 18·07 |
| 10 H | 10 | 2·54 | 2·53 |
| 2 Ag | 216 | 54·82 | 54·52 |
| 12 O | 96 | 24·37 | 24·88 |
| $C^{12}H^{10}Ag^2O^{12}$ | 394 | 100·00 | 100·00 |

| *Air-dried crystals.* | | | Engelhardt & Maddrell. |
|---|---|---|---|
| 12 C | 72 | 16·74 | |
| 14 H | 14 | 3·26 | |
| 2 Ag | 216 | 50·23 | 49·94 |
| 16 O | 128 | 29·77 | |
| $C^{12}H^{10}Ag^2O^{12} + 4Aq$ | 430 | 100·00 | |

Lactic acid mixes with *alcohol* in all proportions, and dissolves sparingly in *ether*. (Berzelius, Gay-Lussac & Pelouze.)

The statement of Cap & Henry (*J. Pharm.* 27, 355) that there exists a *lactate of urea*, and that all the urea contained in human urine is in the form of this compound, has been disproved by Lecanu (*Ann. Chim. Phys.* 74, 90) and Pelouze. (*N. Ann. Chim. Phys.* 6, 65.)

Lactic acid coagulates *white of egg* and sweet *milk*. (Gay-Lussac & Pelouze.)

## *Conjugated Compounds.*

### 1. Lactate of Ethyl.

$$C^{20}H^{20}O^{12} = 2(C^{4}H^{5}O),C^{12}H^{10}O^{10}.$$

A. Strecker. *Ann. Pharm.* 81, 247; 91, 355.
Lepage. *J. Chim. méd.* 20, 8; also *J. pr. Chem.* 31, 377.

*Lactic ether, Milchsaures Aethyloxyd, Milchvinester.*

*Preparation.* 1. Dry lactate of lime is distilled with sulphovinate of potash—or better: 1 pt. of lactate of lime and potash (p. 484), with 1·4 pt. of sulphovinate of potash,—the thin, faintly smelling distillate which passes over between 150° and 180°, saturated with chloride of calcium; and the syrupy solution cooled. Crystals are then obtained consisting of $CaCl,C^{20}H^{20}O^{12}$; and these by distillation yield tolerably pure lactic ether. (Strecker.)

2. Four pts. of pulverised lactate of lime are distilled with 5 pts. of rectified spirit and 3 pts. of oil of vitriol, till the contents of the retort begin to turn brown; and the distillate rectified over chloride of calcium, decanted after 24 hours, and rectified. (Lepage.)

Colourless liquid of sp. gr. 1·08 (0·866 according to Lepage,) having a faint odour (like rum, according to Lepage). It does not exhibit a constant boiling point, but the greater portion distils over between 150° and 160°. (Boils at 77°: Lepage.) Vapour-density 4·75. (Strecker.)

*Calculation.*

| | | |
|---|---|---|
| 20 C | 120 | 50·85 |
| 20 H | 20 | 8·47 |
| 12 O | 96 | 40·68 |
| $C^{20}H^{20}O^{12}$ | 236 | 100·00 |

| | Vol. | Density. |
|---|---|---|
| C-vapour | 20 | 8·3200 |
| H-gas | 20 | 1·3860 |
| O-gas | 6 | 6·6558 |
| Vapour | 4 | 16·3618 |
| | 1 | 4·0904 |

The very unusual condensation to 4 volumes would seem to imply that the rational formula of lactic acid is $C^{10}H^{10}O^{6} = C^{4}H^{5}O,C^{6}H^{5}O^{5}$; but as lactic acid appears in all its other compounds to be bibasic, it may perhaps be supposed that the ether $C^{20}H^{20}O^{12}$ splits up when heated into 2 volumes of $C^{10}H^{10}O^{6}$. (Strecker.)

Lactic ether is neutral to vegetable colours (Strecker), and remains so after keeping for a month in bottles containing air (Lepage); but when mixed with water it immediately exhibits an acid reaction. (Strecker.) With fixed alkalis it is resolved into alcohol and a lactate of the alkali, and when shaken up with milk of lime, it solidifies in the course of a night into a white jelly of lactate of lime. (Lepage.) When the aqueous mixture is boiled with oxide of zinc, alcohol is formed, and lactate of zinc crystallises out on cooling. No ethylolactic acid appears to be formed. (Strecker.) — When dry ammoniacal gas is passed into a solution of lactic ether in absolute alcohol, lactamide is formed, and remains in colourless crystalline laminæ when the solution is evaporated. (Strecker.)

*Lactic ether with Chloride of Calcium.* $CaCl,C^{20}H^{20}O^{12}$. — Lactic ether dissolves a considerable quantity of fused chloride of calcium, with rise of temperature, and, after a while, the mass solidifies in an aggregate of transparent, colourless, crystalline grains, which appear to be rectangular prisms. When heated, they give off lactic ether. (Strecker.)

| | | | | Strecker. |
|---|---|---|---|---|
| 20 C | 120·0 | 41·2 | | 40·6 |
| 20 H | 20·0 | 6·9 | | 6·8 |
| Cl | 35·4 | 12·2 | 19·2 | 12·9 |
| Ca | 20·0 | 6·9 | | |
| 12 O | 96·0 | 32·8 | | |
| $CaCl,C^{20}H^{20}O^{12}$ | 291·4 | 100·0 | | |

Lactic ether mixes in all proportions with water, alcohol and vinic ether. (Strecker, Lepage.)

A mixture of 4 pts. lactate of lime, 5 pts. wood-spirit, and 3 pts. oil of vitriol does not yield any lactate of methyl, when distilled, nothing but wood-spirit passing over. (Lepage.)

## 2. Lactone. ?

$C^{20}H^{16}O^{8}$.

Pelouze. *N. Ann. Chim. Phys.* 13, 262.

The anhydride which remains when lactic acid is distilled at 130°, yields at 150° a distillate, consisting of lactone and lactide, from which the lactone may be distilled off at 130°. It is then washed with a small quantity of water, (in which a portion dissolves) separated therefrom by a pipette, placed in contact with chloride of calcium, whereby the 2 At. water of hydration which it contains, are with difficulty withdrawn, and rectified.

Colourless or pale yellow liquid, which floats on water, boils at about 92°, has a peculiar aromatic odour and burning taste.

Lactone gradually acquires a darker colour by exposure to the air. It burns readily with a blue flame, and without depositing charcoal.

It combines intimately with water, forming an oily hydrate, $C^{20}H^{16}O^8.2HO$, which dissolves with tolerable facility in water. (Pelouze.)

[This product, which Engelhardt was not able to obtain by the same process, cannot certainly be classed with the ketones (vii, 214), since lactic acid, regarded as monobasic, would yield the ketone $C^{10}H^{10}O^6$; $2C^6H^6O^6 - C^2H^2O^6 = C^{10}H^{10}O^6$; moreover there is no known instance of a ketone being formed from a bibasic acid, and lactic acid could scarcely yield one having the composition $C^{20}H^{16}O^8$.]

*Appendix to Lactic Acid.*

## Sarcolactic Acid.

Berzelius. *Schw.* 10, 145.
Liebig. *Ann. Pharm.* 62, 278, and 326.
Engelhardt. *Ann. Pharm.* 65, 259.
W. Heintz. *Pogg.* 75, 391.

Berzelius, in 1806, discovered in muscular flesh, an acid, which he pronounced to be identical with the acid of sour milk, but which, though similar to lactic acid in composition and appearance, nevertheless, as Liebig showed in 1847, exhibited remarkable differences in its salts, and therefore until these differences are explained, perhaps by the discovery of an impurity in the acid of flesh, the latter must be distinguished as sarcolactic acid (paralactic acid, according to Heintz). Berzelius thought that he had detected this acid in many other animal substances, both solid and liquid, viz., in brain, blood, and urine; subsequent researches (p. 473), have however thrown doubt on this conclusion. (Berzelius dissolved in alcohol, the portion of these substances which was soluble in alcohol and in water; added oil of vitriol diluted with a large quantity of alcohol to precipitate the sulphates of potash and soda; digested the filtrate with carbonate of lead; treated the liquid filtered from sulphate, chloride, and often phosphate of lead, with sulphuretted hydrogen; and evaporated the filtrate to a syrup.) Peretti's acid from flesh (*J. Pharm.* 12, 274,) is, according to his later experiments, (*J. Pharm.* 14, 536,) lactic acid containing phosphate of lime.

*Preparation.* 1. The red liquid expressed from chopped flesh is coagulated by heat; the filtrate evaporated to a brown extract; this extract exhausted with alcohol of sp. gr. 0·833; the potash, soda, and lime precipitated from the filtrate as tartrates by alcoholic tartaric acid; the filtered liquid digested with finely triturated carbonate of lead till a portion of the lead is dissolved; the liquid again filtered to separate chloride and tartrate of lead; the alcohol evaporated; the residue dissolved in water; and the lead precipitated by sulphuretted hydrogen.

The liquid filtered from this precipitate, yields, by evaporation, a colourless, very acid syrup, contaminated only with an extractive animal matter. (Berzelius, *Lehrb. Ausg.* iii, 9, 573.) — 2. After the inosate of baryta, &c. (p. 119,) has been deposited from the juice of flesh, the decanted mother-liquor is further evaporated over the water-bath; the residue treated with alcohol, which dissolves all the sarcolactates; the alcoholic solution decanted from the syrup below it, and evaporated to a yellow syrup, which, after 10 days, solidifies in a white crystalline mass, containing — together with a large quantity of sarcolactate of potash present as mother-liquor — creatine, cratinine, and the potash-salt of a peculiar azotised acid. This crystalline mass is mixed with an equal volume of dilute sulphuric acid, (formed of 1 vol. oil of vitriol and 2 vols. water,) or with a quantity of concentrated oxalic acid sufficient to form a crystalline deposit; the mixture immediately treated with 3 or 4 times its volume of alcohol, to precipitate sulphate or oxalate of potash; the filtrate mixed with ether, till this liquid no longer produces turbidity; and the filtrate distilled and evaporated over the water-bath to a syrup. This syrup is washed with half its volume of alcohol, then with 5 volumes of ether; the ethereal solution evaporated and mixed with milk of lime till a strong alkaline reaction is produced; the filtrate left to evaporate in a warm place, till it solidifies into a white crystalline magma; this substance washed with cold alcohol till all yellowish colour is removed from it; the crystals dissolved in hot 60 per cent. alcohol ; and the solution filtered from the sulphate of lime, (decolorised if necessary by animal charcoal,) and evaporated. It then yields the pure potash-salt, from which, by precipitating with sulphuric acid, exhausting the evaporated filtrate with ether, and evaporating the ether, the pure acid may be obtained. (Liebig.) — 3. To obtain the acid from the flesh of fish, especially of pike, with which the process (2) does not succeed, the flesh-juice prepared in the manner described at page 251, vol. x, is evaporated to a syrup, and mixed with an aqueous solution of tannin; the liquid, after separation from the thick yellowish white precipitate, which becomes pitchy when heated, is concentrated, and mixed with sulphuric or oxalic acid; the process continued as in (2); and, finally, an ethereal solution obtained, containing gallic acid (formed from the tannin,) and sarcolactic acid; and from this solution, by evaporation, digestion with milk of lime, (without separating the crystallising gallic acid,) filtering (treating with animal charcoal if necessary,) and evaporating, pure sarcolactate of lime is obtained. (Liebig.)

*Sarcolactic acid* agrees perfectly with lactic acid in external appearance, uncrystallisability, and solubility in water, alcohol, and ether. (Engelhardt & Maddrell.)

*Lime-salt.* — The crystals which separate from hot alcohol contain 29·0 p. c. (10 At.) water; but those which are obtained from water by cooling or spontaneous evaporation, contain from 25·50 to 25·53 per cent. (8 At.); the crystals with 10 At. water obtained from alcohol are likewise converted into the octo-hydrated crystals by crystallisation from water. They, however, exhibit the same form and properties, and the same behaviour when strongly heated, but give off their water at 100°, much more slowly than the crystals of lactate of lime their 10 atoms; and they dissolve in 10·4 pts. of cold water (lactate of lime in 9·5 pts.,) and like the latter in all proportions of boiling water and alcohol. (Engelhardt & Maddrell.)

| *At* 100°. | | | Liebig. |
|---|---|---|---|
| 12 C | 72 | 33·03 | 32·83 |
| 10 H | 10 | 4·59 | 4·68 |
| 2 CaO | 56 | 25·69 | 25·65 |
| 10 O | 80 | 36·69 | 36·84 |
| $C^{12}H^{10}Ca^{2}O^{12}$ | 218 | 100·00 | 100·00 |

| *Air-dried crystals from water.* | | | Liebig. |
|---|---|---|---|
| $C^{12}H^{10}Ca^{2}O^{12}$ | 218 | 75·17 | |
| 8 HO | 72 | 24·83 | 25·55 |
| $C^{12}H^{10}Ca^{2}O^{12}$ + 8Aq | 290 | 100·00 | |

*Magnesia-salt.* — The crystals contain 8 At. water, (those of the lactate only 6 At.,) and dissolve much more readily in water than alcohol. (Engelhardt & Maddrell.)

*Zinc-salt.* — The acid saturated with carbonate of zinc yields, by evaporation, crystals which give off their 13·45 p. c. (4 At.) water (Liebig), 12·9 if they have been obtained by cooling, 13·43 if by spontaneous evaporation (Engelhardt & Maddrell), 13·04 (Heintz), (whereas the crystals of lactate of zinc contain 6 At.,) very slowly at 100°, more quickly at 120° (Heintz). They dissolve in 5·7 pts. of cold, in 2·88 pts. of boiling water, in 2·23 pts. of cold, and nearly the same quantity of boiling alcohol, therefore both in water and in alcohol much more abundantly than lactate of zinc. (Engelhardt & Maddrell.)

| *Dried between* 100° *and* 120°. | | | Liebig. | Heintz. |
|---|---|---|---|---|
| 12 C | 72·0 | 29·70 | 29·40 | 29·44 |
| 10 H | 10·0 | 4·13 | 4·14 | 4·24 |
| 2 ZnO | 80·4 | 33·17 | 33·31 | 33·41 |
| 10 O | 80·0 | 33·00 | 33·15 | 32·91 |
| $C^{12}H^{10}Zn^{2}O^{12}$ | 242·4 | 100·00 | 100·00 | 100·00 |

*Lead-salt.* — The acid saturated at a boiling heat with excess of hydrated lead-oxide, deposits by gradual evaporation, a small quantity of lead-oxide, and if further evaporated after filtration, leaves a clear gum, which, after continued drying at 120°, appears hard and fissured in the cold, but runs together again when heated.

| *Dried at* 120°. | | | Heintz. |
|---|---|---|---|
| 12 C | 72 | 18·65 | 18·15 |
| 10 H | 10 | 2·59 | 2·62 |
| 2 PbO | 224 | 58·03 | 58·87 |
| 10 O | 80 | 20·73 | 20·36 |
| $C^{12}H^{10}Pb^{2}O^{12}$ | 386 | 100·00 | 100·00 |

*Nickel-salt.* — Its crystals, like the lactate, contain 6 At. water, which however they give off completely even at 100°. (Engelhardt & Maddrell.)

*Copper-salt.* — Small, hard, sky-blue nodules. After drying in the air, they give off only 3·7 p. c. water over oil of vitriol, even after

several weeks, and at 100° they very slowly yield 8·96 p. c. water, sintering together at the same time, and assuming a brownish colour; afterwards they become greenish, and then contain 32·87 p. c. cupric oxide. Finally, at 140°, they give off 14 per cent. in all, but the residue on being dissolved in water, leaves a considerable quantity of cuprous oxide. The air-dried crystals dissolve in 1·95 pts. of cold, 1·24 of boiling water, and are much more soluble in alcohol than cupric lactate. (Engelhardt & Maddrell.)

*Silver-salt.* — The dilute acid saturated with precipitated and still moist oxide of silver, then filtered in the dark, and evaporated over oil of vitriol in vacuo, yields, with strong efflorescence, and only when nearly all the water has gone off, white crystals which blacken even in diffused daylight. When dried in vacuo, they turn yellowish at 80°, diminishing in weight by nearly 1·5 per cent., but without any peculiar decomposition; at 100°, they become dark coloured and cake together. From their solution in warm alcohol, they separate almost completely on cooling, not however in the crystalline form, like lactate of silver, but in the form of a translucent jelly, even when a large quantity of alcohol is used. (Heintz.)

| *Crystals dried at* 80°. | | | Heintz. |
|---|---|---|---|
| 12 C | 72 | 18·27 | 18·26 |
| 10 H | 10 | 2·54 | 2·59 |
| 2 Ag | 216 | 54·82 | 54·64 |
| 12 O | 96 | 24·37 | 24·51 |
| $C^{12}H^{10}Ag^2O^{12}$ | 394 | 100·00 | 100·00 |

*Oxygen-nucleus* $C^{12}H^{10}O^8$.

## Anhydrous Lactic Acid.

$C^{12}H^{10}O^{10} = C^{12}H^{10}O^8,O^2$.

PELOUZE. (1845.) *N. Ann. Chim. Phys.* 13, 257; also *N. J. Pharm.* 7, 1; also *Ann. Pharm.* 53, 112; also *J. pr. Chem.* 35, 128.
ENGELHARDT. *Ann. Pharm.* 70, 221.

*Lactic Anhydride, Acide lactidique.* (Laurent.)

*Preparation.* Lactic acid is heated for some time in a retort to 130° (Pelouze), or for a shorter time to between 180° and 200° (Engelhardt), till no more aqueous lactic acid passes over.

*Properties.* Pale yellow, solid, amorphous mass, very easily fusible; (Pelouze), melts below 100°, and may be drawn out into threads on cooling (Engelhardt); has an extremely bitter taste. (Pelouze, Engelhardt.)
According to Pelouze, it is $= C^{12}H^{10}O^{10}$.

*Decompositions.* 1. Dry distillation (p. 480). — 2. It is converted slowly in damp air, and instantly in contact with aqueous alkalis, into ordinary lactic acid. (Pelouze.) It decomposes carbonate of baryta or carbonate of lime but slowly, even when boiled with water. (Engelhardt.) — 3. It absorbs 2 At. ammonia (Pelouze, p. 471).

*Combinations.* The anhydrous acid boiled for a short time with water, dissolves but sparingly, and separates almost completely, with milky turbidity, on cooling; the water however remains bitter. (Engelhardt.)

It dissolves in all proportions in *alcohol*, both hydrated and absolute, and is precipitated therefrom in flakes which gradually unite in drops. (Engelhardt).—It dissolves readily in *alcohol* and *ether*. (Pelouze.)

*Primary-nucleus* $C^{12}H^{20}$.

*Oxygen-nucleus* $C^{12}H^{10}O^{10}$.

## Mucic Acid.

$$C^{12}H^{10}O^{16} = C^{12}H^{10}O^{10},O^{6}.$$

SCHEELE. (1780.) *Opusc.* 2, 111.
HERMBSTÄDT. *Crell. N. Entd.* 5, 31. — *Crell. Ann.* 1784. 2, 509.
TROMMSDORFF. *A. Tr.* 17, 59. — *N. Tr.* 7, 13.
LAUGIER. *Ann. Pharm.* 72, 81; also *Gilb.* 42, 228.
MALAGUTI. *Ann. Chim. Phys.* 60, 195; 63, 86.—*Compt. rend.* 22, 854.
LIEBIG. *Pogg.* 31, 344. — *Ann. Pharm.* 26, 160.
LIEBIG & PELOUZE. *Ann. Pharm.* 19, 258.
HAGEN. *Pogg.* 71, 531.
J. W. JOHNSON, *Ann. Pharm.* 94, 224.

*Schleimsäure, Milkzuckersäure, Acide mucique, Acide sacchlactique.*

*Formation.* Together with oxalic and saccharic acid, in the decomposition of milk-sugar (Scheele), of various kinds of gum (Fourcroy & Vauquelin), and picromel (Thénard), by hot nitric acid. The less hot and the more dilute the nitric acid, the greater is the quantity of mucic, and the smaller the quantity of oxalic and carbonic acid produced, those acids arising from the decomposition of a portion of the mucic acid. (Liebig, *Pogg.* 31, 348.) The gums which yield mucic acid are: Gum-arabic, gum-tragacanth, Bassora-gum, linseed-gum, frankincense, myrrh, opoponax and gum-ammoniacum. (Fourcroy & Vauquelin.)

*Preparation.* Milk-sugar or gum is heated in a retort with 6 pts. of dilute nitric acid, till the whole of the nitric acid is distilled over; as the residue cools, the mucic acid is deposited, and the mother-liquor yields an additional quantity by repeated evaporation and cooling. — The acid separated from the mother-liquor is freed from adhering oxalic and

saccharic acid by washing with a small quantity of cold water and perhaps by again dissolving it in hot water, filtering and crystallising. The oxalate of lime produced when gum is used remains in the filter; it may likewise be removed by repeatedly treating the product with weak nitric acid. 1 pt. of milk-sugar yields about $\frac{1}{4}$ pt. of mucic acid. (Scheele, Fourcroy & Vauquelin, Trommsdorff, Laugier.) — When 1 pt. of milk-sugar is heated with 2 pts. of nitric acid of sp. gr. 1·42, till violent action is set up, then removed from the source of heat, and only gently warmed towards the end of the action, a quantity of mucic acid is obtained amounting to between 60 and 65 per cent. of the acid. (Guckelberger, *Ann. Pharm.* 64, 348.) — Proust mixes the impure acid obtained from gum with a slight excess of ammonia and boiling water till it is dissolved, evaporates the filtrate nearly to dryness; washes the crystallised mucate of ammonia with cold water till it is decolorised; dissolves it in boiling water; and precipitates the mucic acid from it by means of cold dilute nitric acid.

*Properties.* White, sandy, crystalline powder, which reddens litmus and has a slightly acid taste. (Scheele.) The powder consists of microscopic oblique rhombic prisms, sometimes with truncated lateral edges, so that rectangular prisms are formed. (Wackenroder, *J. pr. Chem.* 23, 208.)

| *Crystalline powder.* | | | Berzelius. | Gay-Lussac & Thénard. | Proust. | Liebig. |
|---|---|---|---|---|---|---|
| 12 C | 72 | 34·29 | 33·43 | 33·69 | 33·33 | 33·92 |
| 10 H | 10 | 4·76 | 5·10 | 3·62 | 4·94 | 4·82 |
| 16 O | 128 | 60·95 | 61·47 | 62·69 | 61·73 | 61·26 |
| $C^{12}H^{10}O^{16}$ | 210 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 |

*Decompositions.* 1. The acid, when heated in a retort, melts, froths, blackens, and yields carbonic acid gas with a little carburetted hydrogen; a watery liquid colourless at first, then yellow, afterwards brown, and containing empyreumatic oil, pyromucic acid, with a small quantity of acetic acid; and a brown acid sublimate of pyromucic acid amounting to $\frac{5}{24}$ of the acid; and leaves charcoal with an almost metallic lustre. (Scheele, Trommsdorff, Houton-Labillardière:

$$C^{12}H^{10}O^{16} = \underbrace{C^{10}H^4O^6}_{\text{pyromucic acid.}} + 2CO^2 + 6HO. \quad \text{(Liebig.)}$$

2. In a red-hot crucible, it burns like an oil. (Scheele.) — 3. By aqueous *iodic acid* at 100°, it is completely resolved into carbonic acid and water. (Millon, *Compt. rend.* 19, 271.) — 4. When distilled with *peroxide of manganese* and *sulphuric acid*, it yields formic acid. (C. G. Gmelin, *Pogg.* 16, 55.) — 5. It is but slightly decomposed by six hours' boiling with strong nitric acid, forming a small quantity of oxalic acid. (Hagen.) — 6. When gently heated with 4 pts. of *oil of vitriol*, it acquires at first a rose, then a carmine colour, then becomes black; and the liquid, if afterwards diluted with water, saturated with carbonate of baryta, and filtered, yields a solution of a salt (mucosulphate of baryta?), which however soon deposits mucate and sulphate of baryta. (Malaguti). —

*Iodide, bromide*, and *chloride* of *phosphorus* do not decompose the acid below 180° (Malaguti); but, according to Lies-Bodart (p. 523), pentachloride of phosphorus produces with mucic acid, a peculiar acid, $C^{12}H^4Cl^2O^8$. — 7. When fused with a large quantity of hydrate of potash, it yields oxalate of potash. (Gay-Lussac, *Pogg.* 17, 171.) — 8. By boiling down with water, it is converted into the isomeric substance paramucic acid. (Laugier, Malaguti). — 9. Heated *potassium* and *sodium* decompose it, with emission of light, into alkali and charcoal. (Gay-Lussac & Thénard.)

*Combinations.* The acid dissolves in 60 pts. of boiling water (Scheele); in 80 pts. (Hermbstädt, Morveau, Trommsdorff); and, according to Scheele, is deposited to the amount of $\frac{1}{4}$ on cooling.

The *Mucates* hitherto known are for the most part *bibasic*, $C^{12}H^8M^2O^{16}$, and dissolve but sparingly in water; acid or monobasic mucates of the alkalis are however known, $C^{12}H^9MO^{16}$, which dissolve more readily.

*Mucate of Ammonia.* — *a. Bibasic.* — By supersaturating the solution of the acid in hot water with carbonate of ammonia, and repeatedly crystallising the crystals which form on cooling, colourless, flat, four-sided prisms are obtained = $C^{12}H^8(NH^4)^2O^{16}$. These crystals become soft and yellow at 220°, and between 220° and 240°, are resolved into water, carbonic acid, carbonate of ammonia, pyromucic acid, and bipyromucamide (x, 405), while small quantities of charcoal and paracyanogen remain. 1. Formation of pyromucic acid :

$$C^{12}N^2H^{16}O^{16} = C^{10}H^4O^6 + 2(NH^3,CO^2) + 6HO.$$

2. Formation of bipyromucamide:

$$C^{12}N^2H^{16}O^{16} = C^{10}N^2H^6O^2 + 2CO^2 + 10HO.$$

Perhaps the pyromucic acid formed as in (1), is converted into bipyromucamide by the action of carbonate of ammonia :

$$C^{10}H^4O^6 + 2(NH^3,CO^2) = C^{10}N^2H^6O^2 + 2CO^2 + 4HO. \quad \text{(Malaguti.)}$$

The salt crystallises in crusts, and tastes slightly saline (Trommsdorff); it has a slightly acid taste, and when heated, first gives off ammonia, and then the decomposition-products of mucic acid. (Scheele.) — The salt dissolves sparingly in cold, more readily in hot water (Trommsdorff), and more easily than paramucate of ammonia. (Malaguti.)

| *Crystals dried at* 110°. | | | Malaguti. |
|---|---|---|---|
| 12 C | 72 | 29·51 | 29·83 |
| 2 N | 28 | 11·47 | 11·39 |
| 16 H | 16 | 6·56 | 6·67 |
| 16 O | 128 | 52·46 | 52·11 |
| $C^{12}H^8(NH^4)^2O^{16}$ | 244 | 100·00 | 100·00 |

Trommsdorff found in it 14·2 per cent. of ammonia.

¶. *b. Monobasic.* — Prepared like the acid potash-salt. (*infra.*) Crystallises in colourless needles or thin prisms. After drying over oil of vitriol, it gives off 7·32 p. c. (2 At.) water, at 100°. More soluble in water than the bibasic salt. Yields by dry distillation the same products

as the bibasic salt, together with a small quantity of a yellow oil, which is soluble in water, appears to boil below 100°, and quickly turns brown when exposed to the air.

| *Dried over oil of vitriol.* | | | | Johnson. |
|---|---|---|---|---|
| 12 C | 72 | .... | 29·39 | |
| 9 H | 9 | .... | 3·67 | |
| $NH^4$ | 18 | .... | 7·35 | ........ 7·27 |
| 16 O | 128 | .... | 52·24 | |
| 2 HO | 18 | .... | 7·35 | ........ 7·32 |
| $C^{12}H^9(NH^4)O^{16}$ + 2Aq | 245 | .... | 100·00 | |

In attempting to prepare this salt on the large scale, Johnson obtained crystals containing less than 2 At. and more than 1 At. oxide of ammonium to 1 At. mucic acid; similar crystals are also formed when a solution of the bibasic salt is evaporated; the bibasic and monobasic salts appear indeed to be capable of crystallising together in variable proportions. ¶.

*Mucate of Potash.* — *a. Bibasic.* — Obtained by neutralising the acid with potash, and cooling. —White granular crystals. They do not give off any water at 100°; but at 150°, they turn yellow and give off 1 At. water; and if they are afterwards dissolved in hot water, the solution again yields transparent, colourless crystals of the original salt, together with a brown mother-liquor which throws down a speculum of silver from ammonio-nitrate of silver when heated with it, but does not contain any saccharic acid. (Hagen.) The crystals dissolve in 8 pts. of hot water and separate almost completely on cooling. (Scheele.) They are insoluble in alcohol. (Trommsdorff.)

| *At* 150°. | | | | Hagen. |
|---|---|---|---|---|
| 12 C | 72·0 | .... | 25·14 | |
| 8 H | 8·0 | .... | 2·79 | |
| 2 KO | 94·4 | .... | 32·96 | ........ 32·26 |
| 14 O | 112·0 | .... | 39·11 | |
| $C^{12}H^8K^2O^{16}$ | 286·4 | .... | 100·00 | |

| *Air-dried crystals.* | | | | Hagen. | Trommsdorff. |
|---|---|---|---|---|---|
| 12 C | 72·0 | .... | 24·37 | | |
| 9 H | 9·0 | .... | 3·05 | | |
| 2 KO | 94·4 | .... | 31·96 | .... 31·91 | .... 31·46 |
| 15 O | 120·0 | .... | 40·62 | | |
| $C^{12}H^8K^2O^{16}$ + Aq | 295·4 | .... | 100·00 | | |

*b. Monobasic.* — 1 pt. of mucic acid neutralised with potash and mixed with 1 pt. more of the acid, yields transparent crystals lighter than the salt *a*, soluble in water, and containing, both in the air-dried state and at 100°, $C^{12}H^9KO^{16}$ + 2 Aq. (Hagen.)

| *Crystals.* | | | | Hagen. | Johnson. |
|---|---|---|---|---|---|
| 12 C | 72·0 | .... | 27·05 | | |
| 11 H | 11·0 | .... | 4·13 | | |
| KO | 47·2 | .... | 17·73 | .... 17·40 | .... 17·77 |
| 17 O | 136·0 | .... | 51·09 | | |
| $C^{12}H^9KO^{16}$ + 2Aq | 266·2 | .... | 100·00 | | |

*Mucate of Soda.* — *a. Bibasic.* — The acid neutralised with carbonate of soda yields by slow evaporation, large, transparent, colourless, efflorescent crystals, which give off 8 At. water at 100°, and obstinately retain 1 At.; the solution rapidly boiled down also deposits a white powder containing 1 At. water. (Hagen.) Trommsdorff obtained a crystalline crust [of the last-mentioned salt ?], which did not give off any water at 100°. The salt dissolves in 122 pts. of water at 19° (Malaguti), and in 5 pts. of boiling water; potash added to the solution throws down mucate of potash. (Scheele.)

| | *At* 100°. | | Hagen. | Trommsdorff. |
|---|---|---|---|---|
| 12 C | 72·0 | 27·33 | | |
| 9 H | 9·0 | 3·42 | | |
| 2 NaO | 62·4 | 23·69 | 23·67 | 22·24 |
| 15 O | 120·0 | 45·56 | | |
| $C^{12}H^8Na^2O^{16}$ + Aq | 263·4 | 100·00 | | |

| | *Crystals.* | | Hagen. |
|---|---|---|---|
| 12 C | 72·0 | 21·47 | |
| 17 H | 17·0 | 5·07 | |
| 2 NaO | 62·4 | 18·60 | 18·73 |
| 23 O | 184·0 | 54·86 | |
| $C^{12}H^8Na^2O^{16}$ + 9Aq | 335·4 | 100·00 | |

¶. *b. Monobasic.* — Prepared like the corresponding potash-salt. Crystallises in colourless shining prisms which give off water and become opaque when exposed to the air. After being quickly dried between paper, they give off 22·15 p. c. (7 At.) water at 100°. (Johnson.)

| | *Crystals.* | | Johnson. |
|---|---|---|---|
| 12 C | 72·0 | 24·39 | |
| 9 H | 9·0 | 3·05 | |
| NaO | 31·2 | 10·57 | 10·75 |
| 15 O | 120·0 | 40·65 | |
| 7 HO | 63·0 | 21·34 | 21·15 |
| $C^{12}H^9NaO^{16}$ + 7Aq | 295·2 | 100·00 | |

¶.

*Mucate of Lithia.* — Small, white, shining accuminated crystals, slightly efflorescent, easily soluble in water. (C. G. Gmelin.)

*Mucate of Baryta.* — The acid precipitates chloride of barium in the cold, according to Scheele, slightly, according to Trommsdorff, not at all, according to Hagen. It forms with baryta-water a precipitate soluble in excess of acid. (Thénard.) Mucate of ammonia forms in the cold, if the sides of the vessel are scratched with a glass rod, a precipitate which increases considerably on boiling; the mixture of the acid with chloride of barium forms a copious precipitate on addition of ammonia. (Hagen.) Mucate of potash added to chloride of barium, immediately throws down a heavy, white, tasteless powder, which is insoluble in cold and very sparingly soluble in boiling water. (Trommsdorff.)

| *Dried at* 100°. | | | Hagen. | Trommsdorff. |
|---|---|---|---|---|
| 12 C | 72·0 | 19·34 | | |
| 11 H | 11·0 | 2·96 | | |
| 2 BaO | 153·2 | 41·16 | 41·20 | 42·1 |
| 17 O | 136·0 | 36·54 | | |
| $C^{12}H^8Ba^2O^{16} + 3Aq$ | 372·2 | 100·00 | | |

*Mucate of Strontia.* — The acid forms with strontia-water, a precipitate which dissolves in excess of the acid. (Thénard.) Mucate of potash throws down from strontia-water, a white tasteless powder, insoluble in cold, sparingly soluble in boiling water, and containing 33 p. c. strontia. (Trommsdorff.)

*Mucate of Lime.*—The acid precipitates chloride of calcium (Scheele), slightly (Trommsdorff), not at all (Hagen.) With lime-water, it forms a precipitate soluble in a larger quantity of the acid. (Thénard.) Mucate of ammonia forms with chloride of calcium, a precipitate soluble in acetic acid; and mucate of potash forms with it, an abundant, white, tasteless powder, which when heated, gives off vapours smelling like burnt tartar, then blackens and glows; it is nearly insoluble in water and in aqueous mucic acid. (Trommsdorff.)

| *Dried at* 100°. | | | Hagen. | Trommsdorff. |
|---|---|---|---|---|
| 12 C | 72 | 26·18 | | |
| 11 H | 11 | 4·00 | | |
| 2 CaO | 56 | 20·36 | 20·49 | 21·9 |
| 17 O | 136 | 49·46 | | |
| $C^{12}H^8Ca^2O^{16} + 3Aq$ | 275 | 100·00 | | |

*Mucate of Magnesia.* — The acid does not precipitate sulphate of magnesia. (Trommsdorff, Hagen; Scheele asserts the contrary.) Mucate of potash does not precipitate sulphate of magnesia. (Trommsdorff.) — 1. Mucate of ammonia soon forms with sulphate of magnesia, a precipitate which increases considerably on boiling, and, after drying at 100°, contains 15·37 p. c. magnesia and therefore 4 At. water. (Hagen.) — 2. The solution formed by boiling the acid with water and excess of carbonate of magnesia, deposits when it becomes nearly neutral, a large quantity of a white powder, very sparingly soluble in cold water, and containing 16·4 per cent. of magnesia. (Trommsdorff.)

*Mucate of Alumina.* — Mucic acid and mucate of potash do not precipitate alum.— Hydrate of alumina dissolves slowly in boiling aqueous mucic acid, forming a rough-tasting liquid which reddens litmus, and on cooling deposits the *neutral* salt, in the form of a white powder nearly insoluble in boiling water, and containing 14 per cent. of alumina; and by further evaporating the mother-liquor, the *acid* salt is obtained in crystalline crusts, which have a rough, sour taste, and dissolve readily in boiling water. (Trommsdorff.)

*Potassio-chromic Mucate.* — *Chromomucate de Potasse.*— By treating bichromate of potash with mucic acid, the salt $KO,Cr^2O^3,C^{12}H^8O^{14} + 7Aq.$ is obtained. (Malaguti, *Compt. rend.* 16, 457.)

Mucic acid does not precipitate *manganous* sulphate, or sulphate of *zinc*, or *protochloride of tin*. (Scheele.)

*Mucate of Lead.* — *a. Sexbasic ?* — 1. The salt *b* is converted, by digestion with ammonia, into an unctuous salt, which absorbs carbonic acid from the air. (Berzelius.) — 2. Mucate of ammonia throws down from subacetate of lead, an unctuous salt, sparingly soluble in water, which however is contaminated with a basic acetate of lead, so that its amount of lead varies from 62 to 79 per cent. (Hagen.)

*b. Bibasic.* — The free acid, and the acid combined with alkalis, throws down from nitrate, chloride or acetate of lead, a white powder, insoluble in water. (Scheele, Berzelius, *Ann. Chim. Phys.* 94, 310; Hess, *Ann. Pharm.* 30, 312.)

| *At* 150°. | | | | Hagen. |
|---|---|---|---|---|
| 12 C | 72 | .... | 17·31 | |
| 8 H | 8 | .... | 1·92 | |
| 2 PbO | 224 | .... | 53·85 | 54·10 |
| 14 O | 112 | .... | 26·92 | |
| $C^{12}H^8Pb^2O^{16}$ | 416 | .... | 100·00 | |

| | | | | Berzelius. | Trommsdorff. | Hess. | Hagen. |
|---|---|---|---|---|---|---|---|
| 12 C | 72 | .... | 16·59 | | | | |
| 10 H | 10 | .... | 2·31 | | | | |
| 2 PbO | 224 | .... | 51·61 | 51·61 | 51·5 | 51·37 | 51·51 |
| 16 O | 128 | .... | 29·49 | | | | |
| $C^{12}H^8Pb^2O^{16}$ + 2Aq | 434 | .... | 100·00 | | | | |

*Ammoniacal Mucate of Lead.*—The boiling aqueous solution of mucamide added to neutral acetate of lead mixed with ammonia, throws down the salt $NH^3,C^{12}H^6Pb^2O^{16}$ + 6 Aq., which is decomposed by sulphuretted hydrogen into sulphide of lead and monobasic mucate of ammonia. (Malaguti.)

*Ferrous Mucate.* — Mucate of ammonia or soda (not the free acid, according to Scheele) throws down from oil of vitriol, a yellow powder, which is permanent in the air at ordinary temperatures, but between 150° and 160° turns brown and afterwards takes fire. Dried at 100°, it contains 23·5 per cent. of ferrous oxide, and is therefore $C^{12}H^8Fe^2O^{16}$ + 4 Aq. (Hagen.)

*Cupric Mucate.* — *a. Quadrobasic ?* — Produced when an excess of the carbonate is boiled with the aqueous acid, in the form of an apple-green, insoluble powder, containing 42·92 per cent. of cupric oxide. (Trommsdorff.) — *b. Bibasic* — The ammonia or potash salt, but not the free acid (Trommsdorff) throws down from cupric sulphate, a bluish white powder insoluble in water, which, at 100° contains 27·96 p. c. cupric oxide, and is therefore $C^{12}H^8Cu^2O^{16}$ + Aq. (Hagen.)

*Mercurous Mucate.* —Mucic acid forms an abundant white precipitate with mercurous nitrate. (Scheele, Malaguti.) — The precipitate obtained with mucate of potash, after being washed in the dark and dried at 100°,

is a soft white powder having a metallic taste; it contains 65·08 p. c. of mercurous oxide (63·13 according to Harff); blackens quickly when exposed to light; blackens when heated, yielding carbonic acid, carbonic oxide, mercury and charcoal: and is insoluble (nearly insoluble, according to Harff) in water. (Burckhardt, *N. Br. Arch.* 11, 269.) — Aqueous ammonia separates from the salt a black tasteless powder, which contains 82·11 p.c. mercurous oxide and likewise mucate of ammonia. (Harff, *N. Br. Arch.* 5, 297.)

*Mercuric Mucate.* — Mercuric oxide is insoluble in mucic acid. By precipitating mercuric acetate with mucate of potash, and washing, a soft white powder is obtained, which has a repulsive metallic taste, contains, 48·28 p. c. mercuric oxide at 100°; does not blacken by exposure to light; turns yellow when heated, and is then dissolved into carbonic acid, mercury, and charcoal; it yields metallic mercury when boiled with ammonia; emits fire with heated potassium, and is insoluble in water, alcohol, and ether. (Burckhardt, *N. Br. Arch.* 11, 271.) — The salt is converted by ammonia, into a white powder having a metallic taste, and containing 71·81 p.c. mercuric oxide. (Harff, *N. Br. Arch.* 5, 298.)

*Mucate of Silver.* — Mucic acid forms a white precipitate with nitrate of silver (Scheele), white and gummy (Malaguti), yellowish white. (Hess.) Mucate of potash forms a more yellow precipitate, but of like composition (Hess); mucate of ammonia forms a white precipitate. (Malaguti.) — The air-dried precipitate does not give off anything at 100°, but turns reddish. (Malaguti.)

| | | | Malaguti. | Liebig & Pelouze. | Hagen. |
|---|---|---|---|---|---|
| 12 C | 72 | 16·99 | | | |
| 8 H | 8 | 1·88 | | | |
| 2 Ag | 216 | 50·94 | 50·73 | 50·55 | 51·01 |
| 16 O | 128 | 30·19 | | | |
| $C^{12}H^8Ag^2O^{16}$ | 424 | 100·00 | | | |

Mucic acid is insoluble in *alcohol.*

### *Conjugated Compounds of Mucic Acid.*

## Mucate of Methyl.

$$C^{16}H^{14}O^{16} = 2C^2H^3O,C^{12}H^8O^{14}.$$

MALAGUTI. *Ann. Chim. Phys.* 63, 94.

*Methylic mucate, Mucate de Methylène, Schleimformester.*

Prepared with wood-spirit like mucate of ethyl.

Colourless tasteless crystals, sometimes having the form of rectangular prisms and laminæ, sometimes of six-sided prisms derived from rhombic prisms.

The crystals which separate from boiling water have a density of 1·53; the pulverulent crystals which separate from boiling alcohol have a density of 1·48 at 20°.

| | | Crystals. | Malaguti. |
|---|---|---|---|
| 16 C | 96 | 40·34 | 40·7 |
| 14 H | 14 | 5·88 | 5·9 |
| 16 O | 128 | 53·78 | 53·4 |
| $C^{16}H^{14}O^{16}$ | 238 | 100·00 | 100·0 |

Mucate of methyl begins to decompose at 165°, giving off a black oil, but without fusing; then at 174°, it melts into a black liquid, and gives off with intumescence a gas containing carbon.

It dissolves very readily in boiling water, and in 200 pts. of boiling alcohol. (Malaguti.)

## Mucate of Ethyl.

$C^{20}H^{18}O^{16} = 2C^4H^5O,C^{12}H^8O^{14}$.

MALAGUTI. (1836.) *Ann. Chem. Phys.* 63, 86. — *Compt. rend.* 22, 854.

*Mucic ether, Ethylic* or *Vinic mucate, Schleimvinester.*

*Preparation.* A mixture of 1 pt. mucic acid and 4 pts. oil of vitriol is heated till it assumes a rose-red, then a carmine colour, and ultimately turns black; it is then, after being set aside for 12 hours in a close vessel, mixed with 4 pts. of alcohol of sp. gr. 0·814, without cooling; the crystallised mass, after 24 hours, strongly shaken up with alcohol; afterwards thrown on a filter; and the dirty white crystals remaining thereon, dried and purified by crystallisation from boiling alcohol or water.

*Properties. a.* Crystallised from boiling alcohol. Transparent, colourless, right four-sided prisms, of sp. gr. 1·17 at 20°; at 158°, they melt and give off a small quantity of brown oil; solidify in the crystalline form at 135°, and then after cooling to 70°, melt at 150°. They are tasteless at first, but leave a bitter after-taste. — *b.* Crystallised from hot water: Right rhombic prisms with two broad and two narrow lateral edges; sp. gr. 1·32 at 20°; they melt at 158°, solidify at 122°, and then, after cooling to 70°, melt into an oily liquid at 100°, and completely at 132°; in all other respects they resemble the crystals *a*.

| | | | Malaguti. | Liebig & Pelouze. |
|---|---|---|---|---|
| 20 C | 120 | 45·11 | 45·58 | 45·36 |
| 18 H | 18 | 6·77 | 6·87 | 6·86 |
| 16 O | 128 | 48·12 | 47·55 | 47·78 |
| $C^{20}H^{18}O^{16}$ | 266 | 100·00 | 100·00 | 100·00 |

Liebig & Pelouze (*Ann. Pharm.* 79, 258) mention also an analysis of this compound by Fremy, which agrees with the above.

*Decompositions.* 1. Mucic ether blackens when heated to 170°, then gives off alcohol, water, carbonic acid, pyromucic acid which partly sublimes, a hydrocarbon and acetic acid, and leaves charcoal. — 2. Dry *chlorine gas* converts the melted ether, without any remarkable action, into a mass which no longer crystallises on cooling, but solidifies in the form of a resin, soluble in an equal weight of moderately heated alcohol, and not forming any precipitate with nitrate of silver. — 3. Dry *ammoniacal gas* does not act upon mucic ether heated merely to the melting point, but at 170° produces alcohol, carbonate of ammonia, and a very aromatic oil which dissolves slowly in water. But in aqueous ammonia the ether is immediately converted into mucamide. (*Compt. rend.* 22, 854):

$$C^{20}H^{18}O^{16} + 2NH^3 = C^{12}N^2H^{12}O^{12} + 2C^4H^6O^2.$$

4. Mucic ether is resolved, by long boiling with water, into mucic acid and alcohol, more quickly by boiling with aqueous potash or soda, and immediately, with precipitation, by cold baryta, strontia or lime-water.

*Combinations.* — The ether *b* dissolves in 44 pts. of water at 20°, very readily in hot water, from which it crystallises on cooling.

It dissolves at 15·5°, in 156 pts. of alcohol of sp. gr. 0·814, and very readily in boiling alcohol; it is insoluble in ether. (Malaguti.)

## Ethylomucic Acid.

$$C^{16}H^{14}O^{16} = C^4H^6O^2,C^{12}H^8O^{14}.$$

MALAGUTI. (1846.) *Compt. rend.* 22, 857.

*Mucovinic acid, Weinschleimsäure.*

In the preparation of mucic ether, it sometimes happens that the not quite pure aqueous solution suddenly emits a strong odour of alcohol, turns sour, and leaves on evaporation a residue very different from mucic ether. This residue is freed from admixed mucic ether by repeated washing with alcohol, and crystallised three times from water; it is then no longer rendered turbid by addition of ammonia, in consequence of the presence of mucamide.

White crystals resembling asbestus, having the form of rectangular prisms, and a very sour taste.

The acid melts with decomposition at 190°, and then, on cooling, solidifies in a vitreous mass, which after a while becomes soft and opaque. Its aqueous solution, boiled with oxide of silver, gives off carbonic acid, and forms a silver-compound which detonates when slightly heated.

The acid dissolves with tolerable facility in *water*.

When heated, it absorbs a little more than 1 At. *ammoniacal gas*, with rise of temperature and formation of a tasteless salt, $NH^3,C^{16}H^{14}O^{16}$, which reddens litmus slightly, and dissolves very readily in water.

The solution of this salt forms with the salts of barium, strontium, lead, copper, and silver, precipitates soluble in acetic acid; with lime-salts, a slight precipitate; with magnesia and zinc-salts, none.

The acid dissolves very sparingly in *alcohol*. (Malaguti.)

*Acids isomeric with Mucic Acid.*

## 1. Paramucic Acid.

$C^{12}H^{10}O^{10},O^{6}$.

Laugier (1809). *Ann. Chim. Phys.* 72, 81; also *Gilb.* 42, 228.
Malaguti. *Ann. Chim. Phys.* 60, 197; also *J. Pharm.* 21, 640; also *Ann. Pharm.* 15, 179; also *J. pr. Chem.* 7, 85.

*Acide paramucique.*

*Formation and Preparation.* 1. Mucic acid dissolved in boiling water is evaporated till there remains a yellow and brown viscid mass which hardens and becomes crystalline on cooling. (Laugier.) — 2. Boiling water saturated with mucic acid is evaporated to dryness, the residue dissolved in alcohol, and the alcohol left to evaporate. (Malaguti.)

*Properties.* Rectangular tables united in crusts, more acid (much more, according to Laugier,) than mucic acid; after drying in the air, they do not suffer any further loss at 100°. (Malaguti.)

| | *Crystals.* | | Malaguti. |
|---|---|---|---|
| 12 C | 72 | 34·29 | 34·62 |
| 10 H | 10 | 4·76 | 4·86 |
| 16 O | 128 | 60·95 | 60·52 |
| $C^{12}H^{10}O^{16}$ | 210 | 100·00 | 100·00 |

*Decompositions.* 1. The acid is decomposed by dry distillation, like ordinary mucic acid, yielding pyromucic acid. — 2. Its solution in boiling water yields on cooling ordinary mucic acid, no longer soluble in alcohol, and but sparingly soluble in water. (Malaguti.)

*Combinations.* — The acid dissolves in 73·6 pts. of cold and in 1·73 pts. of boiling water. (Malaguti.) It is more soluble in water than mucic acid. (Laugier.)

The *Paramucates* are more soluble in water than the mucates. Their solutions in boiling water deposit mucates on cooling.

A saturated solution of the acid in boiling water, neutralised with ammonia, deposits the *Ammonia-salt*, even while hot, in delicate white rectangular tables, which are nearly insoluble in boiling water; the ammonia-salt is in fact the only paramucate which is less soluble than the corresponding mucate. When an aqueous solution of the acid saturated at the boiling heat, is neutralised with potash or soda, crystals of

paramucate of potash or soda are obtained by evaporation; but the same solution, if left to cool, deposits crystals of the mucate. The paramucate dissolves in 81·6 pts. of water at 19°.

The acid mixed with *mercurous* nitrate forms, after a while only—in which respect it differs from mucic acid,—a curdy (not gummy) precipitate.

The *silver-salt* contains 48·7 per cent. of silver. (Malaguti.) This amount would agree better with the formula $C^{12}H^{10}Ag^2O^{18}$ than with $C^{12}H^8Ag^2O^{16}$ (Liebig); but in that case the formula of the acid should be $C^{12}H^{12}O^{18}$. (Gm.)

The acid is soluble in *alcohol*. (Laugier, Malaguti.)

## 2. Saccharic Acid.

$$C^{12}H^{10}O^{16} = C^{12}H^{10}O^{10},O^6$$

SCHEELE. *Opusc.* 2, 203; abstr. *Ann. Pharm.* 8, 36.
TROMMSDORFF. *N. Tr.* 2, 1.
GUERIN-VARRY. *Ann. Chim. Phys.* 49, 280.—*Ann. Chim. Phys.* 52, 318; also *Schw.* 68, 371; also *Ann. Pharm.* 8, 24; abstr. *Pogg.* 29, 44.—*Ann. Chim. Phys.* 65, 332; also *J. Pharm.* 23, 416.
ERDMANN. *Ann. Pharm.* 21, 1; also *J. pr. Chem.* 9, 257; 15, 480.
HESS. *Pogg.* 42, 247; also *Ann. Pharm.* 26, 1; also *J. pr. Chem.* 15, 463.—*Ann. Pharm.* 30, 302; also *J. pr. Chem.* 17, 379.
THAULOW. *Ann. Pharm.* 27, 113; also *Pogg.* 44, 497; also *J. pr. Chem.* 15, 465.
LIEBIG. *Ann Pharm.* 30, 313.
HEINTZ. *Pogg.* 61, 315; abstr. *J. pr. Chem.* 32, 267.

*Artificial Malic acid, Metaweinsäure* (Erdmann); *Hydroxalic acid, Ac. oxalhydrique* (Varry). *Zuckersäure*.—Scheele obtained this acid by decomposing sugar and other compounds with nitric acid, and regarded it as identical with malic acid; its separate identity was afterwards established by Hess.

*Formation.* By heating sugar, starch, and many other compounds with a quantity of nitric acid less than sufficient to convert them completely into oxalic acid.—The same or a similar acid is obtained, according to Lowitz (*Crell. Ann.* 1792, 1, 222) in the decomposition of glucose or gum-sugar by alkalis.

*Preparation.* 1. One part of cane-sugar is heated with 3 parts of nitric acid of sp. gr. 1·25 to 1·3, in a capacious basin, till the first bubbles of nitrous gas make their appearance, whereupon the vessel is removed from the fire till the violent action has subsided, and the whole has cooled to 50°; and the liquid is maintained at this temperature over a slow fire, and stirred (above 50°, oxalic would be produced, even by the action of more dilute nitric acid,) till it no longer exhibits a greenish colour, or emits nitrous fumes; it is then diluted, after cooling, with half its bulk of water, neutralized with carbonate of potash, and supersaturated with a quantity of acetic acid, sufficient to render the odour of that acid plainly perceptible, whereby the bibasic saccharate of potash is converted into the monobasic salt, but is not further decomposed: the

monobasic saccharate slowly crystallises out after the lapse of days or perhaps of weeks. These crystals (amounting to 6 per cent. of the sugar,) are dried between paper, and repeatedly crystallised from hot water till they are colourless; their solution then neutralised with potash, and mixed at the boiling heat, with sulphate or nitrate of cadmium; the mixture boiled for some time, the precipitated saccharate of cadmium well washed and decomposed by sulphuretted hydrogen; the filtered aqueous acid evaporated to dryness in the water-bath, and the residue completely dried by leaving it for six weeks in vacuo over oil of vitriol. (Heintz.) — If the potash-salt were converted into the baryta-salt, and the latter decomposed by sulphuric acid, the saccharic acid would turn brown when evaporated, if even a trace of sulphuric acid were present; and if the quantity of sulphuric acid were deficient, the saccharic acid would remain contaminated with saccharate of baryta, which could not be removed by means of alcohol. If the potash-salt were precipitated by a lead-salt, the precipitate would retain a portion of the lead-salt, and this acid would remain associated with the saccharic acid, when the lead-salt was decomposed by sulphuretted hydrogen. (Heintz.)

2. Sugar is distilled with an equal weight of nitric acid, till the liquid acquires a brown colour; the residue neutralised with carbonate of lime, and filtered from the oxalate of lime; the saccharate of lime precipitated by alcohol, washed with alcohol, and dissolved in water; the solution precipitated by acetate of lead; and the lead precipitated decomposed by sulphuretted hydrogen. (Scheele.) Donovan obtained by this process different products, according to the degree to which the action of the nitric acid was carried.

3. The solution of sugar in heated nitric acid of sp. gr. 1·2 is saturated with chalk; the filtrate precipitated by alcohol; the precipitate washed with alcohol; the aqueous solution decomposed by nitrate of lead; and the washed precipitate decomposed by dilute sulphuric acid, and decolorised with animal charcoal. (Trommsdorff.) — One pt. of gum arabic is heated with 2 pts. of nitric acid of sp. gr. 1·38 and 2 pts. of water, till nitrous fumes begin to escape; the liquid then removed from the fire till it has become quiet, afterwards gently heated for an hour, diluted with a four-fold quantity of water, and exactly neutralised with ammonia; the oxalic acid precipitated by nitrate of lime; the reddish yellow filtrate precipitated by acetate of lead; the washed precipitate decomposed by sulphuretted hydrogen or sulphuric acid; the yellow filtrate evaporated and neutralised with ammonia; the resulting black crystals of saccharate of ammonia decolorised with animal charcoal; the solution precipitated by acetate of lead; the washed lead-precipitate decomposed; and the aqueous acid finally evaporated in vacuo. By this process, gum yields 2·8, sugar 3·5, and starch 3·1 per cent. of saccharic acid. (Guerin-Varry.)

5. One pt. of sugar or gum is digested with 1 pt. of nitric acid and ½ pt. water, till the violent action is over; the liquid neutralised with ammonia (or first with carbonate of lime and then with ammonia), precipitated by chloride of calcium, and filtered from the oxalate of lime; the saccharate of lime precipitated from it by alcohol, and decomposed by carbonate of ammonia; the solution filtered from the carbonate of lime and colouring matter, and precipitated by acetate of lead; the well-washed lead precipitate suspended in water, and decomposed by sulphuretted hydrogen; and this treatment of the acid with ammonia, acetate of lead, and sulphuretted hydrogen, repeated (about 6 times,) till the

sulphide of lead has removed all the colour from the acid, and the liquid no longer turns brown when saturated with ammonia and warmed. The acid is then to be carefully evaporated, which is best effected in vacuo. (Erdmann.) Hess proceeds in a similar manner.

6. The liquid obtained from nitric acid and sugar, is saturated with chalk; the filtrate precipitated with acetate of lead; the precipitate washed, suspended in water and decomposed by sulphuretted hydrogen; the filtrate boiled, first by itself to expel the sulphuretted hydrogen, then for a while with excess of potash; and the brown liquid filtered to separate a black humus-like powder, neutralised with acetic acid, again precipitated by acetate of lead, and digested, whereby the basic acetate of lead becomes easier to wash out. The precipitate is then decomposed by sulphuretted hydrogen, the filtrate evaporated, and half neutralised with potash; and the crystals of monobasic saccharate of potash, which separate after some days, decolorised by boiling with animal charcoal. (Thaulow.) From the potash-salt, the acid may be obtained by means of acetate of lead and sulphuretted hydrogen.

*Properties.* After complete drying in vacuo, the acid forms a colourless, brittle, amorphous mass, which cannot in any way be made to assume the crystalline form. (Heintz.) — Colourless or yellowish gum (Erdmann); after drying in vacuo: colourless syrup, which, when set aside in a close vessel, sometimes deposits crystals [of the ammonia-salt? (Heintz)]. (Varry). Erdmann likewise, by exposing to the air the solution of the gum first formed in a small quantity of water, gradually obtained a few crystals. Brown syrup. (Trommsdorff.) — Has the taste of oxalic acid (Varry), pleasantly sour (Thaulow).

| | *Dry.* | |
|---|---|---|
| 12 C | 72 | 34·29 |
| 10 H | 10 | 4·76 |
| 16 O | 128 | 60·95 |
| $C^{12}H^{10}O^{16}$ | 210 | 100·00 |

This formula is based on the supposition that the lead-salt contains the hypothetical anhydrous acid $C^{12}H^8O^{14}$ (Hess). Varry, in accordance with his analyses of the zinc and lead-salts, assumed for the hypothetical anhydrous acid $C^4H^3O^6$.

Saccharic acid has therefore the same composition as mucic acid, notwithstanding the great differences in their properties. These differences cannot be accounted for by halving the atomic weight of either of the acids, since the result would be the uneven atomic number $C^6H^5O^8$. Neither can it be supposed that mucic acid is bibasic, and saccharic acid, with equal atomic weight, quintobasic; for even if a saccharate with 5 At. base should be discovered, it would doubtless be reducible to a compound of the bibasic salt with 3 atoms of base, inasmuch as 2 At. base are sufficient for the complete neutralisation of the acid. Lastly, the isomerism of tartaric, antitartaric and racemic acid cannot in any way be compared with that of mucic, paramucic and saccharic acid. The explanation of this difficulty must therefore be reserved for future investigation.

*Decompositions.* 1. The acid turns yellow at 100° (Varry); it assumes a light brown colour when dried at the heat of the water-bath. (Heintz.) When heated, either by itself or in combination with alkalies, it does not emit the odour of burnt sugar or tartaric acid. (Heintz, Varry.) — It gives off acid vapours, having the odour of burnt sugar, takes fire, and is quickly carbonised. (Trommsdorff.) — 2. By hot nitric acid, it is readily converted into oxalic acid, with emission of nitric oxide. (Heintz.)

$$C^{12}H^{10}O^{16} + 12O = 3C^4H^2O^8 + 4HO.$$

The conversion into oxalic acid takes place in four weeks, even at ordinary temperatures (Varry); it is always accompanied by formation of carbonic acid and nitric oxide. (Varry, Thaulow.) — 3. The acid distilled with 1 pt. of water, 2 pts. of peroxide of manganese, and $2\frac{1}{2}$ pts. of oil of vitriol, froths up, and yields formic and carbonic acid, (Varry, Thaulow.) 4. Heated with oil of vitriol, it blackens and gives off sulphurous acid. (Heintz.) The clear mixture which it forms with nitrate of silver, deposits silver when boiled (Erdmann, Thaulow); when supersaturated with ammonia, it slowly deposits silver in the cold, but quickly on boiling; and silvers the vessel. (Thaulow, Heintz.) A similar effect is produced by saccharate of potash. (Thaulow.) *Pure* monosaccharate of potash does not precipitate nitrate of silver, even on boiling (Hess, Liebig), but when the dilute mixture is gently heated with a very small quantity of ammonia, a silver speculum is produced. (Liebig.) The acid easily reduces metallic gold from its solution. (Erdmann.) — 6. It does not undergo any alteration when boiled with aqueous potash, but when fused with hydrate of potash at 250°, it is resolved into acetate and oxalate of potash:

$$C^{12}H^{10}O^{16} = 2C^4H^4O^4 + C^4H^2O^8.$$

But the fused mass when heated with sulphuric acid emits the odour of butyric as well as of acetic acid. (Heintz.) — 7. The dilute aqueous acid (not the concentrated, according to Heintz), soon becomes covered with mould. (Varry, Heintz.) — Saccharic acid is not susceptible of the vinous fermentation (Trommsdorff); neither is any alteration observed when saccharate of lime is left in contact with casein. (Dessaignes, *N. J. Pharm.* 25, 29.)

The former statement of Erdmann that saccharic acid is identical with fused tartaric (metatartaric) acid, and changes into ordinary tartaric acid, slowly when dissolved in water, more quickly on the addition of a small quantity of alkali, has since been withdrawn by its author. (*J. pr. Chem.* 15, 480.)

*Combinations.* The dry acid quickly becomes viscid by contact with the air, and dissolves very readily in water. (Heintz.) When evaporated in vacuo, it remains in the form of a thick, colourless and inodorous syrup, of sp. gr. 1·416 at 10°, and when dried in contact with excess of oxide of lead, gives off 5·65 per cent. of water; by absorbing moisture from the air, the syrup is reduced to the specific gravity 1·375, with a boiling point of 105°. (Varry.)

The *Saccharates* are *bibasic* or *neutral* salts, having a neutral reaction, dissolving sparingly in water, but easily in saccharic acid, and $= C^{12}H^8M^2O^{16}$, and *monobasic* or acid *salts*, $= C^{12}H^9MO^{16}$, which redden litmus and dissolve with facility. The sparingly soluble salts separate on cooling from boiling water in flakes, which when heated cake together into a viscid mass hardening as it cools.

*Saccharate of Ammonia.* — *a. Bibasic.*— The acid supersaturated with ammonia dries up in vacuo over oil of vitriol to a gum whose solution in cold water is neutral. (Heintz.) Not crystallisable, easily soluble. (Varry.)

*b. Monobasic.* — The aqueous solution of *a*, heated as long as it gives off ammonia, yields on cooling, four-sided prisms, which redden litmus, and dissolve less easily. (Heintz.) Transparent, colourless,

slightly acid, four-sided prisms, with dihedral summits. They are permanent in the air, begin to decompose and assume a yellow colour at 110°, and dissolve in 82 pts. of water at 15°, and in 4 pts. of boiling water. They are insoluble in cold alcohol, but dissolve in hot alcohol. (Varry.)

| | *Crystals prepared by Varry.* | | Thaulow. | Heintz. |
|---|---|---|---|---|
| 12 C | 72 | 31·72 | 32·14 | 31·80 |
| N | 14 | 6·17 | 6·20 | 6·17 |
| 13 H | 13 | 5·72 | 5·82 | 5·76 |
| 16 O | 128 | 56·39 | 55·84 | 56·27 |
| $C^{12}H^9(NH^4)O^{16}$ | 227 | 100·00 | 100·00 | 100·00 |

*Saccharate of Potash.* — *a. Bibasic.* — Transparent, oblique rhombic prisms. (Varry.) The acid neutralised with potash, evaporated to a syrup, and then exposed to the air, yields a crystalline crust, which deliquesces only in very damp air. (Heintz.)

| | *Crystalline crust.* | | Heintz. |
|---|---|---|---|
| 12 C | 72·0 | 25·14 | 25·04 |
| 8 H | 8·0 | 2·79 | 2·86 |
| 2 KO | 94·4 | 32·96 | 32·74 |
| 14 O | 112·0 | 39·11 | 39·36 |
| $C^{12}H^8K^2O^{16}$ | 286·4 | 100·00 | 100·00 |

*b. Monobasic.* — An excess of saccharic acid does not throw down any crystals from potash or its salts. (Varry.) The acid mixed with an insufficient quantity of potash, and left for a few days, yields crystals (originally mistaken for cream of tartar) till it solidifies. (Erdmann.) Crystallises also from a mixture of sugar decomposed by nitric acid, with an insufficient quantity of potash. (Hess.) — Transparent, oblique needles, which redden litmus. (Varry.) The crystals obtained as described at page 514, are snow-white, right four-sided prisms, having a strong acid reaction. (Thaulow.) Their aqueous solution should not turn brown on exposure to the air. (Hess.) The salt intumesces considerably when heated, but without fusing, then chars, and finally leaves carbonate of potash. (Heintz.) Dissolves in 89 pts. of water at 7°, easily in hot water. (Heintz.)

| | *Crystals.* | | Hess. | Thaulow. | Heintz. |
|---|---|---|---|---|---|
| 12 C | 72·0 | 29·01 | 28·52 | 29·38 | 28·95 |
| 9 H | 9·0 | 3·62 | 3·60 | 3·78 | 3·74 |
| KO | 47·2 | 19·02 | 18·66 | 18·86 | 18·72 |
| 15 O | 120·0 | 48·35 | 49·22 | 47·98 | 48·59 |
| $C^{12}H^9KO^{16}$ | 248·2 | 100·00 | 100·00 | 100·00 | 100·00 |

This salt neutralised with ammonia, leaves by evaporation in vacuo, a gum which gives off its ammonia when boiled with water.

*Saccharate of Soda.* — *a. Bibasic.* — Does not crystallise. (Varry.) The acid neutralised with carbonate of soda, leaves when evaporated

over the water-bath, a gum which deliquesces in contact with the air, and by slow evaporation, a syrup, with a few extremely small crystals. (Heintz.)

*b. Monobasic.* — Does not crystallise. (Varry, Heintz.)

When monobasic saccharate of potash is neutralised with carbonate of soda, and the liquid left to evaporate, a syrup is obtained together with very small crystals; the same solution evaporated over the water-bath, gradually yields a gum which becomes moist in contact with the air. (Heintz.)

*Saccharate of Baryta.* — *a. Bibasic.* — By precipitating the acid with baryta-water (Thaulow, Heintz), or by precipitating the bibasic (Varry, Erdmann), or the monobasic saccharate of potash (Heintz) with chloride of barium. The free acid does not precipitate baryta-salts. (Erdmann, Thaulow.) — Precipitated cold, it forms flakes (Varry, Heintz); precipitated at the boiling heat, microscopic prisms. (Heintz.) The flakes dissolve to a moderate extent in water (Varry, Heintz); the crystals are nearly insoluble. (Heintz.)

| | | | Heintz. |
|---|---|---|---|
| 12 C | 72·0 | 20·86 | 20·51 |
| 8 H | 8·0 | 2·32 | 2·41 |
| 2 BaO | 153·2 | 44·38 | 43·98 |
| 14 O | 112·0 | 32·44 | 33·10 |
| $C^{12}H^8Ba^2O^{16}$ | 345·2 | 100·00 | 100·00 |

*b. Monobasic.* — The salt *a* dissolves in the aqueous acid (Varry, Thaulow), and yields a gum by evaporation.

*Saccharate of Strontia.* — *a. Bibasic.* — By precipitating saccharate of potash with chloride of strontium. (Varry.)

*b. Monobasic.* — The solution of the salt *a* in the acid yields transparent right prisms. (Varry.)

*Saccharate of Lime.* — *a. Bibasic.* — The acid forms a precipitate with excess of lime-water. (Varry, Thaulow.) Bibasic saccharate of potash precipitates chloride of calcium (Heintz), — after a while only if the solutions are rather dilute. (Erdmann.) The free acid does not precipitate lime-salts. (Erdmann, Thaulow.) Flakes, or from solution in hot water, microscopic rhombic prisms, bevelled with two faces resting on the obtuse lateral edges. Intumesces very strongly when heated. (Heintz.) In the flocculent state, it dissolves to a moderate amount in water, (Varry, Heintz), but after crystallisation, it is nearly insoluble in boiling water. (Heintz.) From its solution in hydrochloric acid, the salt is precipitated by potash, but not by ammonia. (Erdmann.)

| | | | Heintz. |
|---|---|---|---|
| 12 C | 72 | 27·07 | 26·79 |
| 10 H | 10 | 3·76 | 3·66 |
| 2 CaO | 56 | 21·05 | 21·01 |
| 16 O | 128 | 48·12 | 48·54 |
| $C^{12}H^8Ca^2O^{16} + 2Aq$ | 266 | 100·00 | 100·00 |

*b. Monobasic.* — The salt *a* dissolves readily in the acid. (Varry, Thaulow.) Transparent, four-sided prisms. (Varry.)

*Saccharate of Magnesia.—Bibasic.* — When the aqueous solution of the acid or of the monobasic potash-salt is boiled with a quantity of magnesia not quite sufficient to destroy the acid reaction, or when a mixture of the bibasic saccharate of potash with sulphate of magnesia is strongly concentrated by boiling, the salt separates as a white crystalline powder, or in soft white laminæ. When kept for 12 hours between 130° and 160°, it acquires a tinge of yellow, contains in that state 17·74 p. c. of magnesia (therefore = $C^{12}H^6Mg^2O^{16}$) and becomes strongly heated by contact with water. It dissolves very sparingly in cold, somewhat more readily in hot water. (Heintz.)

| *Crystals.* | | | Heintz. |
|---|---|---|---|
| 12 C | 72 | 25·17 | 24·96 |
| 14 H | 14 | 4·90 | 5·03 |
| 2 MgO | 40 | 13·99 | 14·25 |
| 20 O | 160 | 55·94 | 55·76 |
| $C^{12}H^8Mg^2O^{16}$ + 6Aq | 286 | 100·00 | 100·00 |

*Chromic Saccharate.* — Colourless, oblique rhombic prisms, which redden litmus.

*Saccharate of Bismuth.* — The dilute potash-salt added to nitrate of bismuth dissolved in a large quantity of water, throws down flakes, which are not rendered crystalline by boiling, and are somewhat variable in composition, as the following analyses show. They are insoluble in water both hot and cold, and dissolve but sparingly in acids. (Heintz.)

| | | | | Heintz. |
|---|---|---|---|---|
| 12 C | 72 | 10·81 | 10·89 | 13·01 |
| 8 H | 8 | 1·20 | 1·11 | 1·46 |
| 2 $BiO^3$ | 474 | 71·17 | 70·96 | 67·51 |
| 14 O | 112 | 16·82 | 17·04 | 18·02 |
| $C^{12}H^4Bi^2O^{16}$ + 4Aq? | 666 | 100·00 | 100·00 | 100·00 |

*Saccharate of Zinc.* — *Bibasic.* — 1. Zinc is boiled with the aqueous acid, whereupon hydrogen is evolved, and the resulting small crystals are dried at 100°. (Varry, Heintz.) — 2. Sulphate of zinc is precipitated at the boiling heat by bibasic saccharate of potash; the precipitate dissolved in a large quantity of boiling water; the filtrate set aside for some days to crystallise; and the mother-liquor repeatedly charged with salt by boiling, then filtered and cooled. (Heintz.) — The salt reddens litmus slightly, and is insoluble in cold water, sparingly soluble in hot water, more soluble in the acid. (Varry, Thaulow.)

| *At* 100°. | | | Thaulow. | Heintz. |
|---|---|---|---|---|
| 12 C | 72·0 | 26·43 | 26·28 | 25·71 |
| 8 H | 8·0 | 2·94 | 3·06 | 3·24 |
| 2 ZnO | 80·4 | 29·51 | 29·11 | 28·78 |
| 14 O | 112·0 | 41·12 | 41·55 | 42·27 |
| $C^{12}H^8Zn^2O^{16}$ | 272·4 | 100·00 | 100·00 | 100·00 |

| *Crystals.* | | | Heintz. |
|---|---|---|---|
| 12 C | 72·0 | 24·79 | 24·59 |
| 10 H | 10·0 | 3·44 | 3·58 |
| 2 ZnO | 80·4 | 27·69 | 28·14 |
| 16 O | 128·0 | 44·08 | 43·69 |
| $C^{12}H^{8}Zn^{2}O^{16} + 2Aq$ | 290·4 | 100·00 | 100·00 |

*Saccharate of Cadmium.* — *Bibasic.* — The bibasic potash-salt precipitates sulphate or nitrate of cadmium in the cold, in white flakes which are difficult to wash, and when boiled agglutinate together and ultimately harden; but if the solutions are mixed at the boiling heat, and the boiling is continued, the saccharate of cadmium is deposited as a white heavy crystalline powder, easy to wash and appearing under the microscope to consist of needles. The flakes are nearly insoluble in cold, somewhat more soluble in hot water. (Heintz.)

| | | | Heintz. |
|---|---|---|---|
| 12 C | 72 | 22·5 | 22·20 |
| 8 H | 8 | 2·5 | 2·54 |
| 2 CdO | 128 | 40·0 | 40·49 |
| 14 O | 112 | 35·0 | 34·77 |
| $C^{12}H^{8}Cd^{2}O^{16}$ | 320 | 100·0 | 100·00 |

*Saccharate of Lead.* — When the acid (or its potash-salt according to Hess), is boiled with ever so great an excess of oxide of lead, it parts with only 2 At. water, so that $C^{12}H^{8}O^{14}$ remains combined with the oxide. (Hess, Heintz.) The lead-salts cannot well be obtained pure, on account of their tendency to take up nitrate or acetate of lead. (Heintz.)

*a. Polybasic salt, containing acetate of lead.* — *a.* The free acid or its potash-salt is boiled for some time with excess of neutral acetate of lead, the liquid evaporated to a pasty consistence, and the heavy, granular precipitate washed. (Thaulow.) — $\beta$. Saccharate of potash is boiled with excess of neutral acetate of lead (not with oxide of lead, as erroneously stated in *Ann. Pharm.* 30, 306), the liquid freed from the precipitated and melted lead-salt, then evaporated to a pasty mass, and the residue washed. (Hess.) The amount of lead-oxide rises, on boiling with fresh acetate of lead, to 76·66 per cent. (Hess.) — $\gamma$. The salt obtained by operating as in $\beta$, but with the materials in different proportions. (Hess.) The acid in these two salts appears to be altered (Hess); mixed with acetic acid. (Heintz.) — $\delta$. The precipitate *a*, washed with water which has been freed from air by boiling, and dried over oil of vitriol, in order to preserve it from the action of carbonic acid. (Heintz.) It is a variable mixture of saccharate and acetate of lead, and if the air has not been carefully excluded, it also contains carbonate of lead; hence the proportion of carbon in it does not agree with that of saccharic acid. (Heintz.) — $\epsilon$. The salt which separates at first in the preparation of Thaulow's salt *a*, and agglutinates in a resinous mass. (Heintz.)

| | Thaulow. | Hess. | | Heintz. | |
|---|---|---|---|---|---|
| | $\alpha$. | $\beta$. | $\gamma$. | $\delta$. | $\varepsilon$. |
| C | 9·99 | 11·20 | 9·14 | 10·86 | 13·39 |
| H | 0·70 | 1·13 | 0·61 | 1·17 | 1·54 |
| PbO | 77·00 | 72·05 | 80·13 | 76·16 | 66·10 |
| O | 12·31 | 15·62 | 10·12 | 11·81 | 18·97 |
| | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 |

*b. Salt approaching nearly to the bibasic salt, and sometimes containing nitrate of lead.* — The salt precipitated in white flocks on adding saccharic acid to nitrate, neutral acetate, or basic acetate of lead contains 59·66 p. c. oxide of lead and no water. It turns yellow at 120°; and yields, when fused at 135°, globules which assume a red-brown colour at 135°, decompose at 150°, and then leave a charcoal, which, if shaken out of the vessel while hot, scatters itself in red-hot smoking spherules. The salt, even after carbonisation, deflagrates with nitric acid, like gunpowder. With hot oil of vitriol, it gives off an odour of oil of wine, and finally also of sulphurous acid. It is insoluble in cold water, dissolves very sparingly in hot water, from which it is deposited in scales on cooling; it is insoluble in saccharic acid and in alcohol. (Varry.)—The acid throws down from neutral acetate of lead, a white, non-crystalline powder, which is insoluble in cold, sparingly soluble in boiling water, from which it separates in flocks on cooling; it dissolves readily in saccharic and in other acids, as well as in ammonia. (Erdmann.)

*a.* Obtained by boiling the potash-salt with excess of nitrate of lead, decanting the cooling liquid from the resinous flocks which are first deposited, and washing slightly the delicate white six-sided laminæ which afterwards separate. They detonate with slight appearance of fire, even below a red heat, and leave a carbonaceous mass; with protosulphate of iron and oil of vitriol, they exhibit abundance of nitric acid: they are nearly insoluble in water. — $\beta$. The potash-salt precipitated in the cold by nitric acid. — $\gamma$. Precipitated by mixing nitrate of lead at the boiling heat, with excess of saccharate of potash. — $\delta$. The precipitate $\gamma$ dissolved in boiling water, and obtained in the crystalline form as the filtrate cools. (Heintz.)

| | | | Heintz. | | | |
|---|---|---|---|---|---|---|
| | | | $\alpha$. | $\beta$. | $\gamma$. | $\delta$. |
| 12 C | 72 | 9·63 | 10·01 | 17·01 | 14·92 | 16·28 |
| 8 H | 8 | 1·07 | 1·09 | 2·07 | 1·84 | 1·90 |
| 4 PbO | 448 | 59·89 | 59·31 | 54·92 | 59·47 | 55·27 |
| 24 O | 192 | 25·67 | 25·83 | 26·00 | 23·77 | 26·55 |
| 2 N | 28 | 3·74 | 3·76 | | | |
| $C^{12}H^8Pb^2O^{16}+2(PbO,NO^5)$ | 748 | 100·00 | 100·00 | 100·00 | 100·00 | 100·00 |

[The precipitates $\beta$, $\gamma$, $\delta$, are free from nitrate of lead, because that salt was not used in excess in preparing them.]

The acid imperfectly neutralised with ammonia, and added to less than the equivalent quantity of a hot solution of nitrate of lead, throws down a salt containing from 71·15 to 62·48 p. c. oxide of lead; and the acid completely neutralised with ammonia throws down a salt containing from 65 to 68 p. c. oxide. (Erdmann.)

*c. Salt approaching in composition to the monobasic salt.* — The acid incompletely neutralised with ammonia, forms with less than the equivalent quantity of nitrate of lead, a white precipitate which contains from 38·8 to 39·97 p. c. oxide of lead, and dissolves sparingly in water. (Erdmann.) — The free acid precipitates from nitrate of lead, a salt containing from 35 to 37 p. c. oxide of lead, and from alcoholic neutral acetate of lead, a salt containing 37·8 p. c. oxide. (Erdmann.) — The monobasic salt boiled with water melts into a resin containing from 60 to 63 p. c. oxide, and the liquid on cooling deposits a salt containing 37·3 p. c. oxide. The latter dissolved in ammonia, deposits, on boiling, a salt containing 77 p. c. oxide. (Erdmann.)

*Ferrous Saccharate.* — Iron dissolves in the aqueous acid, with evolution of hydrogen (Varry); the resulting solution leaves a gum when evaporated. (Heintz.)

*Ferric Saccharate.* — The yellow solution of ferric hydrate gradually deposits a basic salt; the acid protects ferric oxide from precipitation by alkalis. (Heintz.)

*Cupric Saccharate.* — Hydrated cupric oxide forms with the cold acid a green solution which deposits a white substance when saturated. This body, washed on the filter and dissolved in a large quantity of water, dries up over the water-bath to an amorphous mass. Monobasic saccharate of potash does not precipitate cupric sulphate, even at the boiling heat. (Heintz.) Alkaline saccharates precipitate cupric sulphate after a while. Cupric sulphate mixed with saccharic acid and then with excess of ammonia, does not form a brown precipitate of copper and cupric oxide by boiling with potash, unless the acid still retains some of the brown matter with which it is contaminated. (Erdmann.)

*Mercuric Saccharate.* — White; reddens litmus; nearly insoluble. (Varry.)

*Saccharate of Silver.* — According to Erdmann & Heintz, saccharic acid does not precipitate nitrate of silver, even with the aid of heat; but according to Varry, the precipitation takes place. — Bibasic saccharate of ammonia or potash added to a concentrated solution of nitrate of silver, throws down a white jelly (Erdmann), from which the wash-water extracts a soluble salt, and which, when boiled with the liquid, reduces the silver, with formation of carbonic and oxalic acid. (Erdmann.) The pure potash-salt does not reduce a solution of nitrate of silver, even at the boiling heat, and precipitates it only when highly concentrated; the precipitate then formed consists of thick, white curdy flakes, which increase on addition of ammonia, and crystallise from solution in hot water. (Liebig.) The precipitate consists of white flakes, which, when recently precipitated, dissolve in a larger quantity of hot water, but when boiled with water, are converted into easily washed crystalline laminæ, which dissolve sparingly in cold water, do not blacken by exposure to light, and whose solution in ammonia deposits a silver speculum, slowly in the cold, quickly when heated. (Heintz.)

| *Dried over oil of vitriol at the ordinary temperature.* | | | Heintz. |
|---|---|---|---|
| 12 C | 72 | 16·99 | 16·79 |
| 8 H | 8 | 1·88 | 1·93 |
| 2 AgO | 232 | 50·94 | 54·34 |
| 14 O | 112 | 30·19 | 26·94 |
| $C^{12}H^8Ag^2O^{16}$ | 424 | 100·00 | 100·00 |

Saccharic acid mixes with *alcohol* in all proportions (Varry), readily (Heintz); dissolves sparingly in *ether,* even at the boiling heat; is insoluble in cold, and very sparingly soluble in boiling *oil of turpentine.* (Varry.)

Saccharic acid does not form any compound ether. (Heintz.)

*Oxyamidogen-nucleus* $C^{12}Ad^2H^8O^{10}$.

## Mucamide.

$$C^{12}N^2H^{12}O^{12} = C^{12}Ad^2H^8O^{10},O^2.$$

MALAGUTI. (1846.) *Compt. rend.* 22, 854.

By mixing mucic ether with aqueous ammonia (p. 511).

Crystallises from the aqueous solution on cooling in colourless microscopic rhombic octohedrons, converted into tables by truncation; of sp. gr. 1·589 at 13·5°; tasteless.

The crystals turn brown at 200°; give off a large quantity of water at 208°; soften and melt at 220°, and give off from that point to 240°,—at which temperature, charcoal and paracyanogen remain,—water, bipyromucamide (x, 405), carbonic acid and carbonate of ammonia. — The crystals heated with water in a sealed tube to between 130° and 140°, dissolve as mucate of ammonia.—Their boiling aqueous solution added to neutral acetate of lead mixed with ammonia, throws down ammoniacal mucate of lead (p. 508). — The same solution added to ammoniacal nitrate of silver, throws down a specular deposit of silver.

The crystals dissolve sparingly in boiling *water,* and separate therefrom on cooling. — They do not dissolve in alcohol or in ether. (Malaguti.)

¶. *Appendix to Mucic Acid.*

## Acid. $C^{12}H^4Cl^2O^8$.

LIES-BODART. *Compt. rend.* 43, 391; *Ann. Pharm.* 100, 325.

*Formation.* By the action of pentachloride of phosphorus on mucic acid:

$$C^{12}H^{10}O^{16} + 2PCl^5 = C^{12}H^4Cl^2O^8 + 2HCl + 4HO + 2PO^2Cl^3.$$

*Preparation.* An intimate mixture of 2 At. pentachloride of phosphorus and 1 At. mucic acid is introduced into a glass retort and heated in the oil-bath to 160°, but not higher. Brisk action then takes place at 100°, attended with copious evolution of hydrochloric acid, and after a while the contents of the retort assumed a somewhat brownish colour. The retort is then to be removed from the oil-bath, and left to cool; water added to decompose the remaining pentachloride of phosphorus, the retort being immersed in cold water to prevent too great a rise of temperature; the contents poured into a basin, and mixed with sufficient lime-water to produce alkaline reaction; the mixture then heated to the boiling point, and the liquid after filtration, left to evaporate in a warm place. It then, after a few days, deposits crystals of the lime-salt $C^{12}Cl^2H^2Ca^2O^8$; and on treating the solution of these crystals with acetate of lead, and decomposing the resulting lead-salt with sulphuretted hydrogen, the acid $C^{12}H^4Cl^2O^8$ is obtained in extremely beautiful crystals.

| *Acid.* | | | Lies-Bodart. |
|---|---|---|---|
| 12 C | 72·0 | 34·15 | 33·88 |
| 4 H | 4·0 | 1·89 | 1·97 |
| 2 Cl | 70·8 | 33·61 | 34·05 |
| 8 O | 64·0 | 30·35 | 30·10 |
| $C^{12}H^4Cl^2O^8$ | 210·8 | 100·00 | 100 00 |

| *Silver-salt.* | | | Lies-Bodart. |
|---|---|---|---|
| 12 C | 72·0 | 16·96 | 16·79 |
| 2 H | 2·0 | 0·47 | 0·51 |
| 2 Ag | 216·0 | 50·80 | 50·70 |
| 2 Cl | 70·8 | 16·70 | 16·64 |
| 8 O | 64·0 | 15·07 | 15·36 |
| $C^{12}Cl^2H^2Ag^2O^8$ | 424·8 | 100·00 | 100·00 |

The acid might be regarded as comenic acid (p. 382), in which 2 At. O are replaced by Cl.

The solution of the lime-salt has no action on polarised light (Lies-Bodart).

## 2. Chloropyromucyl.

$C^{10}H^3ClO^4$.

LIES-BODART. *Ann. Pharm.* 100, 327.

Obtained by the action of pentachloride of phosphorus on pyromucic acid:

$$C^{10}H^4O^6 + PCl^5 = C^{10}H^3ClO^4 + HCl + PCl^3O^2.$$

Strongly refracting liquid, which boils at 170°, smells like chloride of benzoyl, and excites tears but not coughing.

| | | | Lies-Bodart. |
|---|---|---|---|
| 10 C | 60·0 | 46·00 | 45·71 |
| 3 H | 3·0 | 2·29 | 2·36 |
| Cl | 35·4 | 27·17 | 27·35 |
| 4 O | 32·0 | 24·54 | 24·58 |
| $C^{10}H^3ClO^4$ | 130·4 | 100·00 | 100·00 |

The compound placed under a bell-jar near a basin containing water, gradually evaporates, and the liquid remaining in the basin leaves pyromucic acid when evaporated:

$$C^{10}H^3ClO^4 + 2HO = HCl + C^{10}H^4O^6.$$

With ammonia it immediately forms pyromucamide (x, 405):

$$C^{10}H^3ClO^4 + NH^3 = HCl + C^{10}NH^5O^4.$$

¶. *Azo-nucleus* $C^{12}N^6H^8O^6$.

## Base obtained from Cratinine.

$$C^{12}N^6H^{10}O^6 = C^{12}N^6H^8O^6,H^2.$$

DESSAIGNES. *Compt. rend.* 41, 1258; *Ann. Pharm.* 97, 341.

*Formation.* By the action of nitrous acid on cratinine or creatine:

$$\underbrace{2C^8N^3H^7O^4}_{\text{cratinine.}} + 14O = C^{12}N^6H^{10}O^6 + 4CO^2 + 4HO.$$

*Preparation.* When nitrous acid gas is passed into an aqueous solution of cratinine, effervescence takes place (arising from escape of carbonic acid); the liquid soon becomes brown and afterwards turbid, and after some hours deposits a considerable quantity of small yellowish crystals, which become thicker by continued immersion in the mother-liquor. These crystals are the nitrate of the base; and on treating their solution with ammonia, the base is precipitated in the form of a white amorphous powder, which may be washed with water and dried. The mother-liquor of the crystals of the nitrate, also yields a certain quantity of the free base when evaporated over lime under a bell-jar. — A small quantity of the free base is also obtained by the action of nitrous acid upon creatine.

*Properties.* Light, coherent, friable, white mass, the powder of which is soft to the touch and becomes electric by friction. Tasteless.

| | | | Dessaignes. |
|---|---|---|---|
| 12 C | 72 | 33·64 | 34·46 |
| 6 N | 84 | 39·29 | 38·14 |
| 10 H | 10 | 4·67 | 5·24 |
| 6 O | 48 | 22·40 | 22·16 |
| $C^{12}N^6H^{10}O^6$ | 214 | 100·00 | 100·00 |

*Decompositions.* The base heated to 100° with hydrochloric acid, is readily decomposed, yielding oxalic acid, chloride of ammonium, and a crystalline substance containing $C^8N^2H^4O^6$:

$$C^{12}N^6H^{10}O^6 + 8HO = C^8N^2H^4O^6 + 4NH^3 + C^4H^2O^8.$$

*Combinations.* The base is insoluble in water. It dissolves in dilute acids when gently heated, and the solutions on cooling yield well crystallised and sparingly soluble salts.

The *hydrochlorate* forms short deeply striated prisms.

| | | | Dessaignes. |
|---|---|---|---|
| 24 C | 144·0 | 24·40 | 25·48 |
| 12 N | 168·0 | 28·40 | 27·40 |
| 29 H | 29·0 | 4·90 | 5·50 |
| 3 Cl | 106·2 | 17·90 | 17·95 |
| 18 O | 144·0 | 24·40 | 23·67 |
| $2C^{12}N^6H^{10}O^6,3HCl + 6Aq$ | 591·2 | 100·00 | 100·00 |

*Platinum-salt.* — Large crystals, which dissolve in water with tolerable facility.

| | | | Dessaignes. |
|---|---|---|---|
| 24 C | 144·0 | 13·08 | 13·06 |
| 12 N | 168·0 | 15·27 | |
| 29 H | 29·0 | 2·63 | 2·83 |
| 3 Pt | 297·0 | 26·99 | 26·34 |
| 9 Cl | 318·6 | 28·95 | 29·31 |
| 18 O | 144·0 | 13·08 | |
| $2C^{12}N^6H^{10}O^6,3HCl,3PtCl^2 + 6Aq$ | 1090·6 | 100·00 | |

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The compound obtained by the action of hydrochloric acid at 100° on the base $C^{12}N^6H^{10}O^6$, crystallises in long shining prisms or laminæ; dissolves slowly in cold water, readily in hot water, and with tolerable facility in ether; has a disagreeable metallic taste; is fusible; may be volatilised without decomposition; burns with flame and without residue; is slightly acid to test-paper, and does not precipitate the salts of lime, baryta, lead-oxide, cupric oxide or zinc-oxide, — or in dilute solution, mercuric chloride or nitrate of silver; but in somewhat concentrated solution, it precipitates nitrate of silver and mercurous nitrate. It is identical with the substance which Liebig found to accompany sarcosine in small quantity (ix, 432; *Ann. Pharm.* 62, 310.)

| | | | Dessaignes. |
|---|---|---|---|
| 8 C | 48 | 37·50 | 37·61 |
| 2 N | 28 | 21·88 | 21·57 |
| 4 H | 4 | 3·12 | 3·69 |
| 6 O | 48 | 37·50 | 37·13 |
| $C^8N^2H^4O^6$ | 128 | 100·00 | 100·00 |

*Addenda to the Amylene-series.*

1. *Chloride of Valeryl*, $C^{10}H^9O^2Cl$. — Obtained by the action of oxychloride of phosphorus on valerate of soda; also by the action of terchloride of phosphorus on monohydrated valerianic acid:

$$3C^{10}H^{10}O^4 + 2PCl^3 = 3C^{10}H^9O^2Cl + 3HCl + 2PO^3.$$

Colourless very mobile liquid, of sp. gr. 1·0005 at 6°. Boils between 115° and 120° under a pressure of 750 mm. Fumes in the air. Decomposed by water, yielding hydrochloric and valerianic acids. (Moldenhauer, *Ann. Pharm.* 94, 102. Gerhardt, *Traité de Chimie organique*, iv, 975).

2. *Bromide of Valeryl*, $C^{10}H^9O^2Br$. — Obtained by the action of terbromide of phosphorus on valerianic acid. Liquid boiling at 143°.

3. *Tribasic Phosphite of Amyl*, $3C^{10}H^{11}O,PO^3$. — Obtained by acting upon amylate of sodium with terchloride of phosphorus in the same manner as for the preparation of the corresponding ethyl-compound (ix, 359).

Neutral oily liquid, having a very offensive odour, even more disagreeable than that of the ethyl-compound, and more easily decomposed by heat. It boils at 236° in an atmosphere of hydrogen.

| | | | Railton. |
|---|---|---|---|
| 30 C | 180·0 | 61·56 | 61·29 |
| 33 H | 33·0 | 11·29 | 11·43 |
| 3 O | 24·0 | 8·21 | 8·48 |
| $PO^3$ | 55·4 | 18·94 | 18·80 |
| $3C^{10}H^{11}O,PO^3$ | 292·4 | 100·00 | 100·00 |

The compound is insoluble in water, but dissolves in alcohol and in ether. (R. Railton, *Chem. Soc. Qu. J.* vii, 219.)

# ERRATA.

| page. | | line. | | | | | |
|---|---|---|---|---|---|---|---|
| 55 | .... | 15 | from top | for | $SO^3$ | read | $2SO^3$. |
| 192 | .... | 11 | — | ,, | $Cl^{12}C$ | ,, | $C^{12}Cl^2$. |
| 242 | .... | 17 | — | ,, | $C^{12}Ad^2Cl^2O^2$ | ,, | $C^{12}Ad^2Cl^2O^2,O^2$. |
| 243 | .... | 8 | from bottom | ,, | $X^3$ | ,, | $X^2$. |
| 278 | .... | 8 | from top | ,, | $Br^4$ | ,, | $BrH^4$. |
| 301 | .... | 9 | from bottom | ,, | $CyH$ | ,, | $CyH^5$. |
| 308 | .... | 25 | — | ,, | $NH^3,H^2$ | ,, | $NH^2,H^2$. |
| 332 | .... | 8 | from top | ,, | $H^2I$ | ,, | $H^{21}$. |
| 362 | .... | 9 | from bottom | ,, | $C^{10}$ | ,, | $C^{30}$. |
| 392 | .... | 11 | from top | ,, | $C^{16}$ | ,, | $C^{12}$. |
| 486 | .... | 22 | — | ,, | $U^2O^2$ | ,, | $(U^2O^2)^2$. |
| 507 | .... | 2 | from bottom | ,, | $C^{12}H^4O^{14}$ | ,, | $C^{12}H^8O^{14}$. |

# REPORT

OF

# THE TENTH ANNIVERSARY MEETING

OF THE

# CAVENDISH SOCIETY.

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The Anniversary Meeting of the Cavendish Society for the year 1857, was held at the rooms of the Chemical Society, No. 5, Cavendish Square, on Monday, the 2nd of March, at three o'clock in the afternoon.

The Chair was taken by Thomas Graham, Esq., F.R.S., President, who called upon the Secretary to read

## THE REPORT OF THE COUNCIL.

"In presenting the Tenth Annual Report to the Members of the Cavendish Society, the Council think the occasion a suitable one for referring to the objects for which the Society was instituted and briefly reviewing the results of its labours. The first proposition for the establishment of this Society was made in 1846, when a Provisional Committee was formed for making known and carrying into effect the objects of the Association. It was felt that a new motive power was required to bring the results of the most eminent labourers in the departments of Chemistry and the allied sciences in different parts of the world, within the reach of those who were engaged in the pursuit or application of Chemistry in this country. Valuable foreign works existed, relating to the Science of Chemistry and its applications, of which there were none equally comprehensive in our language; and the reproduction of such works in a form accessible to the majority of English Chemists was one of the chief objects contemplated in the establishment of the Cavendish Society. In proposing to accomplish this design by the formation of those for whose benefit it was intended into a Publishing Society, it was not contemplated that this body should in any degree supersede or compete with private or professional publishers; but, on the other hand, it was thought probable that by its efforts an increased demand for scientific works would be created, and that in proportion as this result should ensue, the necessity for its continued labours would become less apparent, as there would be a stronger inducement for publishers to undertake the class of works referred to.

"The constitution of the Society was settled, and its active labours commenced, in 1848. Among the works which were then projected were the translations of LEOPOLD GMELIN'S 'Hand-book of Chemistry' and GUSTAV BISCHOF'S 'Elements of Chemical and Physical Geology,' both of which works are steadily progressing towards completion. Added to these, LEHMANN'S 'Physiological Chemistry' and other works of less extent, make the list of books, produced by the Society in nine years, amount to twenty volumes. It was to be anticipated that the production of works of the extent and character of those issued by the Cavendish Society would leave a narrower field for further labour, and render the task of selecting new works more difficult. Such results afford the best indication of the measure of success which has attended the labours of the Society. But the Council, in making this statement, would not have it inferred that they have already exhausted the store of matter available for their purpose. There are several departments of applied Chemistry in reference to which there are abundance of results not hitherto placed in an eligible form before English readers. Mineralogy, Metallurgy, Agricultural Chemistry, and the Chemical branches of Physics, are among this class of subjects, and although there appears to be some difficulty in getting the results required in the form that would be most satisfactory, it is hoped that this difficulty may be overcome. Among works on Metallurgy, a recently published treatise, by PROFESSOR PLATTNER, on the Roasting of Ores, has been favourably reported on, and is now under the consideration of the Council.

"Some delay has occurred in the completion of PROFESSOR BISCHOF'S work, the third and concluding volume of which should have appeared last year. This has arisen from the indisposition of the author who has been suffering from inflammation of the eyes, but it is trusted that this cause will not further interfere with the preparation of the remaining part of the work.

"MR. WATTS is uninterruptedly proceeding with the translation of GMELIN'S 'Hand-book of Chemistry,' the eleventh volume of which is now in the press. The German editors of this work are also making steady progress with the new German edition, so that there seems to be no probability of any delay occurring in the production of at least one volume a-year until its final completion.

"The extension, from year to year, of the works produced by the Society, of many of which there is always necessarily a considerable stock on hand, and the regulations which have from time to time been made for facilitating the accession of new Subscribers without obliging them to take incomplete sets of the works, having greatly increased and complicated the labour attending the distribution of the books, the Council have appointed MR. HARRISON, Bookseller, of 59, Pall Mall, their Agent for attending to this duty, and they trust this arrangement, which involves no additional expense in the management, will contribute to the convenience of Members and the advantage of the Society.

Treasurer's Statement of the Receipts and Expenditure of the Cavendish Society, from the 1st of March, 1856, to the 1st of March, 1857.

## Receipts.

| | | £ | s. | d. |
|---|---|---|---|---|
| | Balance from previous year | 640 | 2 | 10 |
| 7 | Subscriptions for 1848 | 3 | 13 | 6 |
| 1 | Ditto 1851 | 1 | 1 | 0 |
| 9 | Ditto 1852 | 9 | 9 | 0 |
| 24 | Ditto 1853 | 25 | 4 | 0 |
| 25 | Ditto 1854 | 26 | 5 | 0 |
| 58 | Ditto 1855 | 60 | 18 | 0 |
| 321 | Ditto 1856 | 337 | 1 | 0 |
| 155 | Ditto 1857 | 162 | 15 | 0 |
| 27 | Sets Gmelin's 'Inorganic Chemistry' | 56 | 14 | 0 |
| | | £1323 | 3 | 4 |

## Expenditure.

| | £ | s. | d. |
|---|---|---|---|
| Stationery, Postage, Delivery of Books, &c. | 20 | 19 | 1 |
| Insurance | 2 | 5 | 0 |
| Collector's Commission | 11 | 16 | 0 |
| Secretary | 100 | 0 | 0 |
| Editorial expenses | 336 | 10 | 0 |
| Paper | 212 | 16 | 0 |
| Printing | 379 | 13 | 6 |
| Binding and wrapping | 65 | 1 | 0 |
| | 1129 | 0 | 7 |
| Balance in hand | 194 | 2 | 9 |
| | £1323 | 3 | 4 |

I have examined the above statement, and find it correct.

TRENHAM REEKS.

2nd March, 1857.

It was resolved—

"That the Report just read be received, approved, and adopted."

The Meeting then proceeded to the election of Officers for the ensuing year, and the following Gentlemen were declared to have been duly elected:—

## President.

Thomas Graham, F.R.S.

## Vice-Presidents.

Professor Brande, F.R.S.
Earl of Burlington, F.R.S.
Sir James Clark, M.D., F.R.S.
Walter Crum, F.R.S.
John Davy, M.D., F.R.S.
Charles G. B. Daubeny, M.D., F.R.S.
Michael Faraday, D.C.L., F.R.S.
John Graham, Esq.
Henry Beaumont Leeson, M.D., F.R.S.
W. A. Miller, M.D., F.R.S.
Professor Wheatstone, F.R.S.
Colonel Philip Yorke, F.R.S.

## Council.

G. B. Buckton, F.C.S.
Dugald Campbell, F.C.S.
Philip James Chabot, M.A., F.C.S.
Rev. I. P. Dale.
Warren De la Rue, Ph.D., F.R.S.
W. Ferguson, F.C.S.
J. H. Gilbert, Ph.D., F.C.S.
John Hall Gladstone, Ph.D., F.R.S.
A. W. Hofmann, LL.D., F.R.S.
Henry Letheby, M.B.
W. Odling, M.B., F.C.S.
Trenham Reeks, Esq.
Alfred Smee, F.R.S.
John Stenhouse, LL.D., F.R.S.
R. D. Thomson, M.D., F.R.S.
A. W. Williamson, Ph.D., F.R.S.

## Treasurer.

George Dixon Longstaff, M.D., 9, Upper Thames Street.

## Secretary.

Theophilus Redwood, Ph. D., 19, Montague Street, Russell Square, and 17, Bloomsbury Square.

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## Collector.

Mr. Thomas West, 32, Soho Square.

## Agent for the Distribution of Books, &c.

Mr. Harrison, 59, Pall Mall.

It was resolved—

"That HENRY POLLOCK, Esq., PROFESSOR RAMSAY, and DR. ROSCOE, be appointed Auditors for the ensuing year."

The following Resolutions were unanimously adopted:—

"That the thanks of the Meeting be given to the PRESIDENT, TREASURER, and COUNCIL, for their services to the Society."

"That the thanks of the Meeting be given to the HONORARY LOCAL SECRETARIES for their services to the Society."

"That the thanks of the Meeting be given to the CHEMICAL SOCIETY for the use of their rooms on the present occasion."

The Meeting was then adjourned.

THEOPHILUS REDWOOD, SECRETARY,
19, Montague Street, Russell Square,
and 17, Bloomsbury Square.

MARCH 2ND, 1857.

## OBJECTS, &c., OF THE CAVENDISH SOCIETY.

The Cavendish Society was instituted for the promotion of Chemistry and its allied sciences, by the diffusion of the literature of these subjects.

The subscription, constituting membership, is one guinea a-year, to be paid in advance; and the subscription becomes due on the 1st of January of each year. A member is entitled to a copy of every book published by the Society for the year for which he has subscribed, but no member can receive the Society's publications until his subscription has been duly paid.

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## WORKS OF THE CAVENDISH SOCIETY.

1848.

1.—CHEMICAL REPORTS AND MEMOIRS. Edited by Thomas Graham, F.R.S. (Out of Print.)

2.—HAND-BOOK OF CHEMISTRY. By Leopold Gmelin. Translated by Henry Watts, B.A., F.C.S. Vol. I.

1849.

3.—HAND-BOOK OF CHEMISTRY. By Leopold Gmelin. Vol. II.

4.—HAND-BOOK OF CHEMISTRY. By Leopold Gmelin. Vol. III.

5.—THE LIFE AND WORKS OF CAVENDISH. By Dr. George Wilson.

1850.

6.—HAND-BOOK OF CHEMISTRY. By Leopold Gmelin. Vol. IV.

7.—HAND-BOOK OF CHEMISTRY. By Leopold Gmelin. Vol. V.

1851.

8.—PHYSIOLOGICAL CHEMISTRY. By Professor Lehmann. Translated by George E. Day, M.D., F.R.S. Vol. I. (Out of Print.)

9.—HAND-BOOK OF CHEMISTRY. By Leopold Gmelin. Vol. VI.

1852.

10.—HAND-BOOK OF CHEMISTRY. By Leopold Gmelin. Vol. VII. (Organic Chemistry, Vol. I.)

11.—PHYSIOLOGICAL CHEMISTRY. By Professor Lehmann. Vol. II.

12.—ATLAS OF PLATES relating to PHYSIOLOGICAL CHEMISTRY. By Dr. Otto Funke.
(Supplement to Lehmann's Physiological Chemistry.)

1853.

13.—HAND-BOOK OF CHEMISTRY. By Leopold Gmelin. Vol. VIII. (Organic Chemistry, Vol. II.)

14.—ELEMENTS OF CHEMICAL AND PHYSICAL GEOLOGY. By Professor Bischof. Vol. I.

1854.

15.—THE LIFE AND SCIENTIFIC RESEARCHES OF DALTON. By Dr. W. C. Henry, F.R.S.

16.—PHYSIOLOGICAL CHEMISTRY. By Professor Lehmann. Vol. III.

17.—LAURENT'S CHEMICAL METHOD. Translated by Wm. Odling, M.B.

1855.

18.—HAND-BOOK OF CHEMISTRY. By Leopold Gmelin. Vol. IX. (Organic Chemistry, Vol. III.)

19.—ELEMENTS OF CHEMICAL AND PHYSICAL GEOLOGY. By Professor Bischof. Vol. II.

1856.

20.—HAND-BOOK OF CHEMISTRY. By Leopold Gmelin. Vol. X. (Organic Chemistry, Vol. IV.)

21.—A second book for this year will be issued.

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CHEMICAL REPORTS AND MEMOIRS. Edited by Professor Graham. This work is out of print.

GMELIN'S HAND-BOOK OF CHEMISTRY. Translated and Edited by Henry Watts, B.A., F.C.S.

Members of the Cavendish Society, or others through a Member of the Society, may obtain one or more copies of the first Six volumes of this work, comprising the whole of the Inorganic Chemistry, for a Subscription of two guineas.

Members may also have for one year's subscription the Seventh and Eighth Volumes of Gmelin's Hand-book, which are the first two volumes of the part treating of Organic Chemistry.

The Ninth volume of the Hand-book is the first of the books for 1855.

LEHMANN'S PHYSIOLOGICAL CHEMISTRY. Translated and Edited by Dr. G. E. Day, F.R.S.

The First Volume of this work is out of print. There still remain a sufficient number of copies of the Second and Third Volumes, and of Dr. Otto Funke's Atlas of Physiological Plates, for supplying those members who have not completed their sets.

BISCHOF'S ELEMENTS OF CHEMICAL AND PHYSICAL GEOLOGY.

The First Volume of this work having been issued for the year 1853, in conjunction with the Eighth Volume of Gmelin's Chemistry, members who do not possess, and do not desire to subscribe for, the previous volumes of Gmelin, may have the Life and Works of Cavendish instead of the Hand-Book of Chemistry, as the second book for that year. Or the First and Second Volumes of Bischof's Geology may be had for one year's subscription.

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*** Applications for the books of the Society, or for information relating to them, are to be made, if by letter, to the Secretary, or personally to Mr. Harrison, 59, Pall Mall.

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